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Transformation Toughened Ceramics for the Heavy Duty Diesel Engine Technology Program — PHASE II

S. Musikant, S.C. Samanta,
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General Electric Company
Space Systems Division.

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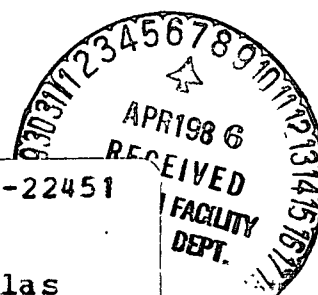
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SECTION 1

INTRODUCTION AND BACKGROUND

The objective of this program is to develop a transformation toughened structural ceramic with improved high temperature properties and scale up the process to sizes representative of components for a heavy duty engine diesel engine.

During the first year (Phase I) of this study, the feasibility of using $\text{ZrO}_2\text{-HfO}_2$ solid solution as a toughening agent in mullite ($3\text{ Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and alumina (Al_2O_3) has been demonstrated. Specimens of mullite and of alumina containing 10-20v/o of $\text{ZrO}_2\text{-HfO}_2$ (1:1 molar) solid solution were fabricated by sintering or hot pressing at 1590-1620°C, characterized and tested for physical, mechanical and thermal properties. Significant toughening of both matrix materials were exhibited.(1)*

Based on the need for a low thermal conductivity and high thermal shock resistant ceramic in advanced diesel engines, transformation toughened (TT) mullite was chosen as the prime candidate material for this study. The second year (Phase II) efforts concentrated on the optimization of processes and scale up for transformation toughened mullite. The material was characterized in sufficient detail to provide the component designer/user a data base necessary for preliminary design.

During the second year (Phase II) effort three tasks plus a reporting task were completed. The three technical tasks are described below:

*Numbers in () refer to references.

Task 1 - Process Optimization

Process variables were investigated to achieve high strength transformation toughened mullite. The variables investigated were:

1. Powder preparation method for mullite matrix material.
2. Powder preparation method for the toughening agent precursor, $Zr_{0.5}Hf_{0.5}O_2$.
3. Composition, namely volume % of the second phase additive or toughening agent $Zr_{0.5}Hf_{0.5}O_2$.
4. Powder milling, blending and cold pressing (including iso-static pressing) procedures.
5. Near net shape consolidation by sintering and/or HIP ing.

The resulting specimens were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Flexural strength or modulus of rupture, compressive strength and fracture toughness of the materials were determined at room temperature as well as at elevated temperatures. The characterizations were repeated for selected specimens after being subjected to a thermal soak in air at $1000^{\circ}C$ for approximately 100 hours.

Task 2 - Process Scale Up

The best process developed in Table 1 was scaled up to a size consistent with a diesel engine component. A typical size to be considered for scale up is a piston cap approximately 5 1/2" O.D. X 1/2" thick. The actual scale up achieved was on the order of 1" X 1" X 6" long.

Billets were fabricated to the scaled up dimensions and test specimens were cut from these billets for detailed characterization.

Task 3 - Characterization

Selected specimens from the scaled up billets were characterized as follows:

1. Microstructure by SEM.
2. Modulus of rupture at RT, 500°C, 800°C, 1000°C.
3. Compressive strength at RT and 800°C.
4. Fracture toughness at RT by indentation technique and fracture toughness at RT, and 800°C by 4 point bend bar with multiple indents.
5. Coefficient of thermal expansion, RT to 1200°C.
6. Thermal conductivity at 110°C, 700°C and 1250°C.

SECTION 2

TRANSFORMATION TOUGHENING (TT)

ZrO₂, HfO₂ and solid solutions of ZrO₂-HfO₂ exist in three crystalline phases. These are a low temperature monoclinic form, a high temperature tetragonal form, and a still higher temperature cubic form. There have been a large number of investigations (2-5) of transformation toughened ZrO₂ and transformation toughening of other ceramic matrices such as Al₂O₃, where ZrO₂ has been used as the toughening compound. Transformation toughening by ZrO₂ depends on the metastable retention of the tetragonal phase upon cooling from elevated temperature and the athermal tetragonal-monoclinic (t→m) transformation of ZrO₂ grains (with an increase in volume) under the influence of an advancing crack. Near the t→m equilibrium temperature, transformation toughening does not occur because the transition takes place thermally. TT is most effective at temperatures far below the equilibrium t → m temperature.

For ZrO₂, the equilibrium temperature for the monoclinic-tetragonal phase transition is about 1000°C (1832°F) during heat up. For HfO₂, m→t transformation occurs at approximately 1749°C (3164°F). As shown in Figure 1, Phase Diagram of the ZrO₂-HfO₂⁽⁶⁾ system, a 1:1 molar ZrO₂-HfO₂ solid solution has a m→t transformation temperature of about 1420°C (2588°F) and thus such a solid solution increases the temperature range (compared to that of ZrO₂ alone) where transformation toughening is effective. In this program, the 1:1 molar ZrO₂-HfO₂ was employed for the most part as the toughening agent. The temperature of interest for engine applications extends to 1371°C (2500°C), although diesel engine operation is generally limited to a temperature <814°C (1500°F).

In summary, transformation toughening (TT) of a consolidated, dense mullite body by inclusions of ZrO₂-HfO₂ solid solution depends on the retention of metastable tetragonal phase of the ZrO₂-HfO₂ solid solution and transformation of metastable tetragonal to the thermodynamically stable monoclinic phase under the influence of an advancing crack. The process is shown schematically in Figure 2.

SECTION 3

EXPERIMENTAL PROCEDURE

3.1 MATERIALS AND PROCESSING

Major raw-materials used for preparation of TT mullite compositions are mullite (the matrix) and $\text{ZrO}_2\text{-HfO}_2$ (1:1 molar) as the toughening phase. High purity mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) powder from Baikowski International Corporation, Charlotte, N.C., was used as the matrix material. Initially Baikowski mullite, Grade 193, was planetary ball milled (PBM), wet, for $1\frac{1}{2}$ hour, dried and then PBM for 15 minutes to get the starting matrix powder. Later on, another new, finer variety of Baikowski mullite, grade 193 CR, became available and thus it was substituted for the mullite used earlier. The data sheet from Baikowski International on 193 CR mullite is shown in Table I. It was found that this mullite powder in the as received condition is equivalent to the old Baikowski mullite (193 grade) after planetary ball milling as described above.

$\text{ZrO}_2\text{-HfO}_2$ solid solution toughening phase powder was prepared from an aqueous solution of zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and hafnium oxychloride ($\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$) in desired proportions via sol-gel process. For the most part, 1:1 molar $\text{ZrO}_2\text{-HfO}_2$ was used as the toughening agent. The method of $\text{ZrO}_2\text{-HfO}_2$ powder preparation by sol-gel technique followed by drying, calcination and planetary ball milling is described in Figure 3. $\text{ZrO}_2\text{-HfO}_2$ powder in other proportions, like, 2:1 molar and 3:1 molar were also prepared in the same manner and each material was used as a toughening phase in a limited number of TT mullite compositions.

TT mullite batch compositions were prepared by planetary ball milling both the mullite matrix and $\text{ZrO}_2\text{-HfO}_2$ toughening phase powders in requisite proportions (90-85/10-15 vol %) for 15-30 minutes. Some batches containing Al_2O_3 additions to the mullite matrix were prepared using Norton Co., grade 38-900 Al_2O_3 . The alumina and mullite were pre-blended by PBM for 15 minutes before milling with the $\text{ZrO}_2\text{-HfO}_2$ powder. A few batches of mullite-1:1 molar $\text{ZrO}_2\text{-HfO}_2$ (90/10 v/o) were also attrition milled in n-propanol for 6-9 hours in order to prepare much finer particle size batch materials.

Powder batches thus prepared were pressed into billets by cold isostatic pressing (CIP) at 40-55 KSI. The billets were then densified by sintering in air at 1600-1650°C for 0.5-1.0 hour, followed by, in some cases, hot isostatic pressing (HIP) at 1500-1650°C, 29-30 KSI argon.

Figure 4 shows various possible fabricating processes for a TT material exercised during this study and the precursor GE IR&D study.

3.2 CHARACTERIZATION

The resulting TT materials were characterized for fraction of retained tetragonal phase by X-ray diffraction (XRD) as described in Reference 1 and microstructure by scanning electron microscopy (SEM). Mechanical properties of selected samples including modulus of rupture, fracture toughness and compressive strength of the materials at room and elevated temperatures were determined. These mechanical tests were performed by Illinois Institute of Technology Research Institute (IITRI), Chicago, Illinois. Modulus of rupture and elastic modulus were determined on TT specimens (3 mm X 4 mm X 45 mm on 20/40 mm supports) by 4-point flexure test as per MIL-STD-1942(MR).

Most of the fracture toughness K_{IC} measurements were performed in 4 point flexure by multiple indent method as per Cook and Lawn⁽⁷⁾.

SECTION 4

RESULTS AND DISCUSSIONS

4.1 PROCESS OPTIMIZATION-MAXIMIZATION OF PERCENT RETAINED TETRAGONAL PHASE

During the initial stage of the investigation, processing of mullite-1:1 $\text{ZrO}_2/\text{HfO}_2$ (90/10 v/o) was optimized in order to achieve high percent retained tetragonal of $\text{ZrO}_2\text{-HfO}_2$ solid solution phase. A high percent retained tetragonal which is transformable is desired to enhance the potential for TT during crack propagation. The mullite matrix powder and $\text{ZrO}_2\text{-HfO}_2$ toughening agent were wet milled for various periods of time in a planetary ball mill to produce starting powder of varying particle sizes and distributions. Ten (10.0) gm batches were prepared by PBM for 15-30 minutes. Three pellets (0.5" diameter) of each powder batch were then cold pressed and sintered at $1610^\circ\text{C}/30$ minutes and percent tetragonal phase retained was determined by XRD. Details of the materials, processing conditions and XRD results are given in Table II. Based on the data, it seemed that further wet milling of the mullite beyond $1\frac{1}{2}$ hours did not show much benefit. However, size reduction of $\text{ZrO}_2\text{-HfO}_2$ toughening phase by extended milling provides some improvement in percent tetragonal phase retainment. The highest result of 34% retained tetragonal was obtained on a mix composition (TT101984B) with $1\frac{1}{2}$ hours milled mullite and 1:1 $\text{ZrO}_2\text{-HfO}_2$ milled for 8 hours. Thus, such starting powders were used for further batch preparation. It was also found (TT020785) that the new, deagglomerated Baikowski mullite, 193 CR, was a good substitute for $1\frac{1}{2}$ hrs PBM mullite, type 193.

Based on the data in Table II, it was also found that percent tetragonal phase retainment was improved to about 40% (TT102984B vs TT101984B) by a two-stage milling operation. Thus, later on this technique was also employed for batch preparation. Results in Table II also show about 49% retained tetragonal for a mullite-2:1 molar $\text{ZrO}_2/\text{HfO}_2$ composition and about 46% retained tetragonal for a mullite-3:1 molar ZrO_2HfO_2 composition.

4.2 SCALE UP-LARGE BILLET PREPARATION AND MICROSTRUCTURAL CHARACTERIZATION

Large amounts (about 400.0 gms each prepared in 10.0 gm batches) of two mullite $\text{ZrO}_2/\text{HfO}_2$ compositions were prepared for large-scale billets for characterization. Billets of mullite and a mullite- ZrO_2 composition were also made for comparison.

Batch compositions, processing methods, sintered density and percent retained tetragonal by XRD of sintered pieces are described in Table III. Each powder batch composition was pressed into a large billet (approx. 8 3/4" X 1 1/4" X 1") by CIP'ing at 40 KSI. The billets were then cut into about 2.5" long pieces and sintered at 1610°C for 30 minutes. XRD studies indicated quite high fraction of tetragonal phase retainment. Figure 5 illustrates the XRD patterns for the ZrO₂-HfO₂ and ZrO₂ containing specimens.

4.3 MECHANICAL PROPERTIES OF TT MULLITE

Test specimens from sintered TT ceramic billets, as mentioned above, were machined and fabricated by BOMAS Machine Specialities, Inc., Somerville, MA. The test specimens were finished and tested in accordance with MIL-STD-1942(MR) by IITRI, Chicago, Illinois, for mechanical properties (4-point flexural strength, elastic modulus and fracture toughness) at room temperature and elevated temperatures (500, 800, 1000°C). They were also characterized for their microstructures by SEM as well as optical microscopy. Table IV shows the test matrix for these TT materials.

Mechanical properties of various TT mullite materials, as described in Table III, are given in Table V. The mullite-10 v% 1:1 ZrO₂/HfO₂ composition showed the best mechanical properties of the various compositions studied. It showed a flexural strength or MOR of about 38.2 KSI at room temperature and 33.3 and 35.4 KSI at 800°C and 1000°C respectively. MOR showed a dip (27.2 KSI) at 500°C probably due to some intrinsic mechanism. This trend was also seen in other compositions. Fracture toughness, K_{IC}, for mullite-10 v% 1:1 ZrO₂/HfO₂ was 2.73 and 2.44 MPa at room temperature and 800°C respectively.

Complete mechanical test results are given in the Appendix I authored by J. W. Adams of IITRI.

4.4 MICROSTRUCTURE AND EDX ANALYSIS

Figures 6 to 9 show SEM fractographs of the fracture surfaces of flexure test specimens (described in Table V) after test at room temperature. Figures 10 to 12 show fracture surfaces after 1000°C flexure tests of mullite, mullite-10 v% ZrO₂ and mullite-10 v% 1:1 ZrO₂/HfO₂ respectively. Figure 13 shows the microstructure of mullite-10 v% 1:1 ZrO₂/HfO₂ after polishing and thermally

etching at 1500°C, 15 mins. It shows round $\text{ZrO}_2/\text{HfO}_2$ solid solution grains $<1\text{ }\mu\text{m}$ and elongated 1-5 μm mullite grains. It is believed finer grain sizes are necessary for further improvement in mechanical properties.

Also, stoichiometry of a mullite-10 vol % 1:1 $\text{ZrO}_2/\text{HfO}_2$ specimen was investigated by energy dispersive X-rays (EDX) analysis. Figure 14 illustrates the difference in composition in the mullite- $\text{ZrO}_2\text{-HfO}_2$ grain-boundary (A) and the mullite grain (B) showing a definite increased silicon peak in the grain boundary.

A quantitative analysis of the mullite- $\text{ZrO}_2\text{-HfO}_2$ grain boundary by EDX shows a Al/Si wt % ratio of 67.2/32.7, which is much lower than a theoretical Al/Si wt % ratio of 74.3/25.7 in a stoichiometric nominal mullite (71.8/28.2 wt % $\text{Al}_2\text{O}_3/\text{SiO}_2$). EDX analysis of other TT materials (Table V) also shows SiO_2 rich mullite compositions which would lead to a SiO_2 -rich glassy phase in grain boundaries at processing temperatures. The presence of such a high silica glassy phase in grain-boundaries is believed to have contributed to degrading the flexural strength of the TT materials tested up to this point in the study.

4.5 IMPROVED TT MULLITE BY USE OF Al_2O_3 -RICH MULLITE MATRIX

In order to minimize the formation of a SiO_2 -rich liquid phase in a TT ceramic at the sintering temperature, it was decided to prepare two Al_2O_3 -rich mullite matrix materials by adding 10 and 18 vol % Al_2O_3 to 193 CR Baikowski mullite. The mullite matrix, #1A, had a calculated composition of about 72.0/28.0 wt % $\text{Al}_2\text{O}_3/\text{SiO}_2$ and another mullite matrix, #2A, had 75.0/25.0 wt % $\text{Al}_2\text{O}_3/\text{SiO}_2$. Phase diagram work by Klug and Prochazka at GE-CRD⁽⁸⁾ has shown that mullite can contain up to 75 wt % Al_2O_3 at 1650°C.

As shown in Table VI density of the sintered TT materials increased by about 1.5 - 2.0% after containerless HIP'ing. Density of the sintered plus HIP'ed materials ranged between 98.0 - 99.0%. Although compositions containing 10 vol % 1:1 $\text{ZrO}_2\text{-HfO}_2$ exhibited higher percent retained tetragonal compared to those containing 15 vol % $\text{ZrO}_2\text{-HfO}_2$, (10 - 11% vs. 5 - 6% of the $\text{ZrO}_2\text{-HfO}_2$ content) after sintering, further processing by HIP'ing resulted in approximately the same percent retained tetragonal (5-6%) for both levels of $\text{ZrO}_2\text{-HfO}_2$ addition

probably due to grain growth. This is considered to be a low percent retained tetragonal, on the order of 0.5% of the total volume of the specimen in the case of the 10 v/o 1:1 $\text{ZrO}_2\text{-HfO}_2$ addition.

4.6 MICROSTRUCTURE OF MULLITE (Al_2O_3 RICH)

We also examined the microstructure of all the TT materials by a scanning electron microscope (SEM). Photomicrographs showing $\text{ZrO}_2\text{-HfO}_2$ solid solution (ss) toughening phase distribution and grain size in these sintered and/or HIP-ed materials are shown in Figures 15 to 19. They show fairly uniform distribution of the toughening phase ($\text{ZrO}_2\text{-HfO}_2$ ss) and sizes range predominantly between 0.2 to 1.0 μm . The first four materials (TT 052025-1 to 4, Table V), which have been sintered and then HIP-ed also show some larger $\text{ZrO}_2\text{-HfO}_2$ ss grains (about 1-3 μm) due to the extended heating cycle compared to TT 061485 specimen, which was made by sintering only.

4.7 DISCUSSION OF MECHANICAL TEST RESULTS

The mechanical test data is presented in full detail in Appendix I. Specimen designations used in Appendix I are described in Table VIIIB.

The results tabulated in Table VIII (billets described in Table VIIIA) show that the addition of 1:1 molar $\text{ZrO}_2\text{-HfO}_2$ solid solution to mullite significantly enhances the MOR at RT and elevated temperatures. The effect on K_{IC} is stronger at both RT and elevated temperature. Thermal soak of these materials at 1000°C/140 hrs shows a RT strength (MOR) degradation of about 25%. Scanning electron microscopy has shown grain growth during such thermal soaks and the strength degradation is attributed to such grain growth.

Of the TT mullite specimens, Specimen #SM6 in Table VIII appears to be about the best of the compositions although additional work is expected to show much improved properties over #SM6. In this specimen fracture toughness was increased by 50% at RT and by 75% at 800°C and MOR was improved by 45% at RT, 30% at 800°C and 10% at 1000°C over straight mullite.

There appears to be a drop-off in strength at temperatures in the 500-800°C range for mullite and the TT-mullites (for example specimens SM1 and SM6).

The compression data for one billet SM11 appears encouraging. As can be seen in Table IX. If one takes the highest data point for each condition, even at the current state of development of the TT-mullite, very high values were measured on single cylindrical test specimens 6.35 mm dia X 12.7 mm long. These test points were: RT 375 Ksi; 800°C 267 Ksi; 1000°C 174 Ksi; and after 1000°C/100 hr thermal soak, RT 178 Ksi.

4.8 SINTERING SCHEDULE VERSUS % RETAINED TETRAGONAL & GRAIN SIZE

Although the highest 4 point flexural strength of about 48 Ksi was obtained with an alumina-rich TT mullite, it is clear that further improvement in mechanical properties of such TT materials is needed. It is believed that still finer grain size is needed to achieve higher strength. Thus, a number of batches of mullite #1A-1:1 molar $\text{ZrO}_2\text{-HfO}_2$ (90/10 v%) were prepared by attrition milling in n-propanol for 9 hours. Powder batches were then CIP'ed into billet form at 55 Ksi and sintered in air at various temperature between 1500-1650°C for 30 minutes. The idea is to keep the grain sizes of the toughening $\text{ZrO}_2\text{-HfO}_2$ phase (as well as matrix phase) small as one in the range which would maximize the percent retainment of the transformable tetragonal phase and hence increase the strength and fracture toughness of the TT material. Density and % retained tetragonal in the sintered TT material(s) are shown in Figure 20. It appears that a sintering temperature of 1600°C will be preferred to 1650°C because percent retained tetragonal reached a maximum of about 23% (at > 96% theoretical density) at 1600°C. In addition, as shown in SEM microstructures in Figure 21, as expected, $\text{ZrO}_2\text{-HfO}_2$ grain sizes are also much smaller at 1600°/30 minutes than those obtained after sintering at 1650°C/30 minutes, approximately 1.0 μm compared to approximately 0.5 μm (Figure 20).

Thus, it is believed that additional optimization in mullite- $\text{ZrO}_2\text{-HfO}_2$ compositions and processing techniques will be effective for further improvement in the mechanical properties of transformation toughened mullite.

4.9 THERMOPHYSICAL

Thermophysical properties of TT materials were not measured during this Phase II study⁽¹⁾. However, thermal expansion coefficient (CTE), thermal diffusivity and thermal conductivity data on various TT mullite and TT alumina determined in Phase (1) are listed in Table IX. The CTE's of the mullite materials were about 60% of those measured for the alumina matrix materials. Also, the thermal conductivity of the mullite matrix specimen was seen to be between 23% and 40% of the comparable alumina matrix specimen over the temperature range (110-1250°C) investigated.

SECTION 5

SUMMARY AND CONCLUSIONS

Transformation toughened (TT) mullite is a good candidate as a structural ceramic component in advanced diesel engine applications due to its low thermal conductivity, low thermal expansion coefficient and inherently high thermal shock resistance. During Phase II of this DOE-NASA sponsored program, attempts were made to develop optimized mullite-ZrO₂/HfO₂ compositions and processes for scale up and characterization in order to provide the component designer/user the data base necessary for design.

Investigations of various mullite-ZrO₂/HfO₂ compositions included processing via preparation of ZrO₂-HfO₂ (1:1 molar) toughening phase by a sol-gel method, planetary ball milling or attrition milling of starting materials and powder batches, cold isostatic pressing into billet form and then sintering or sintering followed by hot isostatic pressing. Characterization of TT materials included percent ZrO₂-HfO₂ solid solution tetragonal phase by X-ray diffraction, density, mechanical properties, MOR or flexural strength, fracture toughness, K_{IC}, elastic modulus, compressive strength at room and elevated temperatures upto 1000°C, thermal expansion and conductivity, and microstructures by scanning electron microscopy.

The best TT material developed so far had a composition of 85 vol % mullite - 15 vol % 1:1 molar ZrO₂-HfO₂ (Specimen SM-6 in Table VIII). The mullite was a modified Baikowski mullite prepared by adding extra Al₂O₃ (Baikowski mullite/Al₂O₃ = 90/10 vol %) in order to eliminate high silica content glassy phase at the grain boundaries and thus improve the mechanical properties.

This mullite - ZrO₂/HfO₂ transformation toughened material showed a 4 point bend flexure strength of 48 KSI and 34 KSI at room temperature and 800°C respectively.

Fracture toughness, K_{IC} , was found to be $3.3 \text{ MPa}\sqrt{\text{m}}$ at room temperature and 2.57 at 800°C . In comparison, untoughened mullite (made by the same process) had a MOR of 33 KSI and K_{IC} of $2.3 \text{ MPa}\sqrt{\text{m}}$ at room temperature and a MOR 26 KSI and K_{IC} , $1.5 \text{ MPa}\sqrt{\text{m}}$ at 800°C (Table X).

However, it has been suggested that a TT material should have at least 60 KSI room temperature flexural strength (4 point bend) to be seriously considered for a piston cap design study for diesel engine as originally planned under Phase III of the current program.

Based on the experimental data obtained so far, it is apparent that further work towards optimization of mullite - $\text{ZrO}_2/\text{HfO}_2$ compositions and processing methods is needed.

RECOMMENDATIONS FOR FUTURE WORK

Such advanced work would be aimed at further reductions in particle size by attrition milling and lowest possible temperature processing. Probably, the best approach would be to cold isostatically press the powder, relatively low temperature sinter (bisque fire), encapsulate, and HIP at the lowest possible temperature, $\sim 1500^\circ\text{C}$.

In addition, all sources of defects such as large pores, large, uncomminuted particles in the batch, and defects in the CIP'ed green body will have to be eliminated since many flexural fracture surfaces during the investigation showed such flaws, as described in Appendix I.

SECTION 6

REFERENCES

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2. "Transformation Toughening, Part 4, Fabrication, Fracture Toughness and Strength of $\text{Al}_2\text{O}_3\text{-ZrO}_2$ Compositions", F. F. Lange, J. Of Materials Science, 17, p. 247-254 (1982).
3. "Design of Transformation Toughened Ceramics", N. Claussen, M. Ruhle, Advances in Ceramics, Vol 3, Science & Technology of Zirconia, American Ceramic Society, 1981.
4. "Stress-Induced Transformation of Tetragonal ZrO_2 Particles in Ceramic Matrices", Nils Claussen, J. Am. Ceramic Society, 61 (1-2) 85-86 (1978).
5. "Transient Thermal Stress Behavior in ZrO_2 -Toughened Al_2O_3 ", J. Am. Ceramic Society, 64 (1) 37-39 (1981).
6. "The System Zirconia - Hafnia", R. Ruh, H. Garrett, N. Tallam and R. Domagela, J. Am. Ceramic Society, 51, p. 23 (1968).
7. "Modified Indentation Toughness Technique", R. F. Cook and B. R. Lawn, J. Am. Ceramic Society, C-200, November 1983.
8. F. J. Klug, PhD Thesis, "Alumina-Silica Phase Equilibria in the Mullite Region", December 1984, Rensselaer Polytechnical Institute.

TABLE I

HIGH PURITY MULLITE
REF. 193 CR(BAIKOWSKI, INTERNATIONAL
CHARLOTTE, NORTH CAROLINA)

Chemical Formula:	$3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
Minimum Purity:	> 99.2%
% Converted to Mullite Phase:	> 98%
Surface Area:	2 m ² /gm
Bulk Density:	0.6 gm/cc
Tap Density:	0.9 gm/cc
Pressed Density:	1.30 gm/cc (2000 psi)

Agglomerate Size Distribution
Cumulative Weight Percent

< 1.0 μ m	24
< 1.5 μ m	34
< 3.0 μ m	85
< 6.0 μ m	100

Mullite can also be supplied in an
as-calcined agglomerated form with
a larger particle size distribution.

TABLE II

DESCRIPTION OF TT MULLITE COMPOSITIONS

SPECIMEN ID	MIX COMPOSITION, VOL % MULLITE	ZrO ₂ -HfO ₂ (1:1 Molar)	PROCESSING CONDITIONS	PERCENT RETAINED TETRAGONAL (BY XRD)
TT101584A	90 (1)	10 (a)	Planetary ball milled (PBM) for 15 minutes; pressed pellets sintered at 1610°C/30 minutes	26%
TT101584B	90 (1)	10 (b)	"	26
TT101784	90 (2)	10 (a)	"	22
TT101884A	90 (3)	10 (a)	"	22
TT101884B	90 (4)	10 (a)	"	20
TT101984A	90 (1)	10 (c)	"	29
TT101984B	90 (1)	10 (d)	"	34
TT101984C	90 (2)	10 (b)	"	22
TT101984D	90 (2)	10 (c)	"	26
TT102294A	90 (2)	10 (d)	"	30
TT102284B	90 (3)	10 (b)	"	22
TT102384A	90 (3)	10 (c)	"	26
TT102384B	90 (3)	10 (d)	"	29
TT102384C	90 (4)	10 (b)	"	18
TT102384D	90 (4)	10 (c)	"	19
TT102384E	90 (4)	10 (d)	"	27
TT102584C	90 (1)	10 (a)	Planetary ball milled for 30 mins. in two stages; first PBM for 15 mins, scraped the powders from mill wall and then PBM for another 15 mins; cold pressed pellets sintered at 1610°C/30 mins.	34
TT102984B	90 (1)	10 (d)	"	40
TT102984A	90 (1)	10 (e)	"	49
TT101284B	90 91)	10 (f)	Same as TT10584A	46
TT020785	90 (5)	(3:1 molar ZrO ₂ -HfO ₂) 10 (d) (1:1 m ZrO ₂ -HfO ₂)	"	40

TABLE II (CONTINUED)

"

NOTES

Mullite (1,2,3,4) - Baikowski mullite, grade 193, planetary ball milled (PBM), wet, 1½, 3, 5 and 8 hours respectively; dried and further PBM 15 minutes.

ZrO₂-HfO₂ (a,b,c,d,) - 1:1 molar ZrO₂-HfO₂ from sol-gel oxychlorides, calcined 750°C/2 hours, wet PBM for 1,2,4 abd 8 hours respectively; dried and then PBM 15 minutes.

ZrO₂-HfO₂ (e) - 2:1 molar ZrO₂-HfO₂ from sol-gel oxychlorides, calcined 750°C/2 hrs, wet PBM for 1 hour, dried and then PBM 15 minutes.

ZrO₂-HfO₂ (f) - 3:1 molar ZrO₂-HfO₂ from sol-gel oxychlorides, calcined 750°C/2 hours, wet PBM for 1 hour, dried and then PBM 15 minutes.

Mullite (5) - Baikowski mullite, grade 193 CR, as-received.

TABLE III

TT BILLETS FOR CHARACTERIZATION

SPECIMEN ID	COMPOSITION, VOL % MULLITE TOUGHENING AGENT	PROCESSING METHOD	DENSITY gms/cc	% THEORETICAL	% RETAINED TETRAGONAL
TT1111584	100 (1) -	Powder batch CIP'ed at 40 KSI, sintered at 1610°C/30 minutes	3.07	96.7	N/A
TT1111684	90 (1) 10 (d) 1:1 m ZrO ₂ -HfO ₂	Two-stage milling in PBM as for TT102984B in Table II; batch CIP'ed at 40 KSI & billet sintered at 1610°C/30 mins	3.55	97.2	40
TT120784A	90 (1) 10 (e) 2:1 m ZrO ₂ -HfO ₂	"	3.49	97.5	66
TT120784B	90 (1) 10 ZrO ₂	"	3.35	97.4	78
TT041285-2	90 (2AA) 10 (d)	Dry PBM 15 min CIP at 60 KSI Sinter 1620C/30 min 1670C/1 hr HIP 1650C/30 KSI/1 hr (Partial melt of specimen during HIP)	- - -	8.86 9.49 99	

TABLE III (CONTINUED)

NOTES

Billet Size as CIP'ed 8 3/4" X 1 1/4" X 1"
Cut billets as sintered 2.1" X 1 1/8" X 7/8"

Mullite (1) - Same as in Table II. Baikowski mullite grade 193 PBM wet 1.5 hrs, dried and PBM 15 mins.

Mullite (2AA) - Baikowski mullite grad 193 Norton alumina 38-900, 80/20 v/o, PBM wet 3 hrs, dried and PBM 15 mins.

1:1 m ZrO₂-HfO₂ (d) - Same as in Table II
PBM wet 8 hrs, dried and PBM 15 mins

2:1 m ZrO₂HfO₂ (e) - Same as in Table II
ZrO₂ - ZIRCAR Zyp ZrO₂, as received

TABLE IV TEST MATRIX

Property	Temperature, °C ^a			
	25	500	800	1000
Flexure strength and elastic modulus				
Unexposed	3	3	3	3
Exposed 100 hr/1000°C	3	3	3	3
Fracture toughness				
Unexposed	3		3	
Exposed 100 hr/1000°C	3		3	
Fracture surface analysis	All samples optically, selected samples in an SEM			

^aNumbers in table represent sample replicates.

TABLE V

MECHANICAL PROPERTIES OF TRANSFORMATION TOUGHENED MULLITE

COMPOSITION	RETAINED TETRAGONAL V/O OF TOTAL	RT			500C			800C			1000C		
		MOR KSI	K _{IC} MPam ^{1/2}	E MPSI	MOR KSI	E PMSI	MOR KSI	K _{IC} MPam ^{1/2}	E MPSI	MOR KSI	K _{IC} MPam ^{1/2}	E MPSI	MOR KSI
Mullite	N/A	33.4	2.33	27.2	23.3	35.6	25.8	1.5	32.1	33.0	32.1	26.0	33.0
Mullite - 10 V/O ZrO ₂	7.8	37.6	3.07	27.6	25.4	29.5	30.4	2.8	23.4	31.2	23.4	-	31.2
Mullite - 10 V/O 2:1 ZrO ₂ / HfO ₂	6.6	34.5*	2.90	28.4*	-	-	-	-	-	29.3	-	19.0	29.3
Mullite - 10 V/O 1:1 ZrO ₂ / HfO ₂	4.0	38.2	2.73	27.6	27.2	33.2	33.3	2.44	27.0	35.4	27.0	20.5	35.4

All test specimens from cold isostatic pressed and sintered billets as in Table III.

Mechanical properties average of three specimens except as noted.

*Two Specimens

4 PT Flexure bar 3 mm X 4 mm C 45 mm on 20.40 mm supports.
MIL-STD-1942 (MR)

K_{IC} by Multiple Indent 4 PT Flexure

TABLE VI
TT MULLITE COMPOSITION BILLETS (ALUMINA RICH)

NO.	COMPOSITION, VO % MULLITE ZrO ₂ -HfO ₂ (1:1 Molar)	PROCESSING CONDITIONS	% THEORETICAL DENSITY	% RETAINED TETRAGONAL*
TT052185-1	85 (1A)	Dry PBM 15 minutes, scrapped mill, PBM 15 mins, CIP-ed at 55 KSI and sintered at 1650°C for 1 hr & then HIP-ed at 1500°C, 29 KSI, ½ hr.	96.8 (Sintered) 98.3 (HIP-ed)	5.6 (Sintered) 5.4 (HIP-ed)
TT052185-2	90 (1A)	"	97.5 (Sintered) 98.8 (HIP-ed)	10.2 (Sintered) 6.0 (HIP-ed)
T052185-3	85 (2A)	Dry PBM 15 minutes, CIP-ed at 55 KSI and then sintered at 1650°C/1 hour & then HIP-ed at 1500°C, 29 KSI, ½ hr.	97.2 (Sintered) 98.7 (HIP-ed)	6.1 (Sintered) 5.3 (HIP-ed)
TT052185-4	90 (2A)	"	97.1 (Sintered) 98.9 (HIP-ed)	10.6 (Sintered) 5.5 (HIP-ed)
TT061485	90 (2A)	Attrition milled in n-propanol for 6 hrs., CIP-ed at 55 KSI and then sintered at 1650°C/1 Hr	97.3	10.0
TT071785	90 (1A)	Attrition milled in n-propanol for 9 hrs, CIP'ed at 55 KSI and then sintered at 1650C/1 hr	97.3	10.1

TABLE VI (CONTINUED)

NOTE:

Mullite (1A) - Baikowski Mullite, 193 Cr/Norton Alumina 38-900 (90/10 V %); Al₂O₃/SiO₂ 72.0/28.0 W/O Calculated
 Mullite (2A) - Baikowski Mullite, 193 CR/Norton Alumina 38-900 (82/18 V %); Al₂O₃/SiO₂ 75.0/25.0 W/O Calculated
 Wet PBM 2 hours, dried and PBM 15 minutes.

ZrO₂-HfO₂(1:1 molar) - Sol-gel oxychlorides, dried, calcined 750°C/2 hours, Wet PBM
 for 8 hours, dried and ground in a mortar and pestle

Sintered billets - Approx. 2¼" X 1" X 5/8"

*As percentage of ZrO₂-HfO₂ Content

TABLE VII

MECHANICAL PROPERTIES OF TT MULLITE (ALUMINA RICH)

COMPOSITION	RETAINED TETRAGONAL V % OF TOTAL	RT			800°C		
		MOR (KSI)	K _{IC} (MPa√m)	E (MPSI)	MOR (KSI)	K _{IC} (MPa√m)	E (MPSI)
Mullite #1A/1:1 m ZrO ₂ -HfO ₂ (85/15 V %)	0.81	48.1	3.3*	32.0	33.8	2.57	34.8
Mullite #1A/1:1 m ZrO ₂ -HfO ₂ (90/10 V %)	0.60	41.9		32.7	22.62	-	32.14
Mullite #2A/1:1 m ZrO ₂ -HfO ₂ (85/15 V %)	0.80	41.1		32.1	26.49	3.02	31.00
Mullite #2A/1:1 m ZrO ₂ -HfO ₂ (90/10 V %)	0.55	31.3		33.9	16.05	2.26	31.14
Mullite #2A/1:1 m ZrO ₂ -HfO ₂ (90/10 V %)	1.0	38.8		31.6	34.22	-	31.42

All data average of 3 test points.

4 Pt flexure bar 3 mm X 4 mm C 45 mm on 20/40 mm supports.

K_{IC} by Multiple Indent 4 Pt Flexure except where noted.

*Single Indent Technique

TABLE VIII

4-PT FLEXURE TEST RESULTS

SPECIMENS 3 X 4 X 45 mm

TEST PER MIL-STD-1942 (MR)

MULLITE 2A/
1:1 ZrO₂-HfO₂
85/15 V/O
#SM 8MULLITE 1A/
1:1 ZrO₂-HfO₂
85/15 V/O
#SM 6MULLITE
1:1 ZrO₂-HfO₂
40/10 V/O
#SM 5MULLITE
#SM 1

RT

MOR (Ksi)

E (Msi)

K_{IC} (MPa m)

33.4

27.2

2.3

39.3

32.6

3.8

48.1

32.0

3.3*

41.2

32.1

500

MOR (Ksi)

E (Msi)

K_{IC} (MPa m)

22.9

34.6

800

MOR (Ksi)

E (Msi)

K_{IC} (MPa m)

25.9

22.6

25.5

33.4

33.8

34.8

26.5

31.0

1000

MOR (Ksi)

E (Msi)

K_{IC} (MPa m)

32.9

25.8

After Thermal Soak
@ 1000°C

36.0

29.1

(140 hrs)

RT

MOR (Ksi)

E (Msi)

K_{IC} (MPa m)

31.9

30.1

All test data avg of 3 tests.

All K_{IC} by 4 point flexure, multiple indent method (Reference 3) except where noted by *

*Single indent method (Reference 4)

TABLE VIIIA
MULLITE - COMPOSITION OF BILLETS

SPECIMEN	COMPOSITION MULLITE	V/O ZrO ₂ -HfO ₂ 1:1 Molar	PROCESSING CONDITIONS	% OF THEORETICAL DENSITY	% RETAINED TETRAGONAL AS % OF ZrO ₂ -HfO ₂	% RETAINED TETRAGONAL AS % OF BILLET
SM1 (TT1111584)	100	0	Powder batch CIP'ed at 40 KSI, sintered at 1610°C/30 minutes	96.7	N/A	N/A
SM5 (TT041285-2)	90	10	Dry PBM 15 min CIP at 60 KSI Sinter 1620C/30 min 1670C/1 hr HIP 1650C/30 KSI/1 hr (Partial melt of specimen during HIP)	99	4.0	0.40
SM6 (TT052185-1)	85 (1A)	15	Dry PBM 15 mins, scrapped mill, PBM 15 mins, CIP-ed at 55 KSI and sintered at 1650°C for 1 hr & the HIP-ed at 1500°C, 29 KSI, ½ hr.	96.8 (S) 98.3 (H)	5.6 5.4	0.84 0.81
SM8 (TT052185-3)	85 (2A)	15	Dry PBM 15 minutes, CIP-ed at 55 KSI and then sintered at 1650°C/1 hour & then HIP-ed at 1500°C, 29 KSI, ½ hr.	97.2 (S) 98.7 (H)	6.1 5.3	0.92 0.80
SM11 (TT071785)	90 (1A)	10	Attrition mill batch in n-propanol 9 hrs, CIP 55 Ksi, sinter 1650°C/ 1 hr	97.3 (S)	10.1	1.01

TABLE•VIIIB

SPECIMEN DESIGNATIONS USED IN APPENDIX I

<u>APPENDIX I DESIGNATION</u>	<u>SPECIMEN NO.</u>	<u>REFERENCE TABLE NO.</u>
SM1	TT111584	III
SM2	TT111684	III
SM3	TT120784A	III
SM4	TT120784B	III
SM5	TT052185-1	III
SM6	TT052185-1	VI
SM7	TT052185-2	VI
SM8	TT052185-3	VI
SM9	TT052185-4	VI
SM10	TT061485	VI
SM11	TT071785	VI

TABLE IX

COMPRESSION TEST RESULTS FOR MULL 1:1 ZH (IITRI SM11)
AT VARIOUS TEMPERATURES

Sample Number	Compressive Strength		Elastic Modulus		Poisson's Ratio
	psi	MPa	10 ⁶ psi	GPa	
<u>25°C</u>					
1	375,250	2587.3	32.6	224.7	0.29
2	144,600	997.0	--	--	--
3	122,200	842.5	26.8	184.6	--
Mean	214,120	1475.6	29.7	204.7	--
<u>800°C</u>					
4	260,710	1797.5	--	--	--
5	266,870	1840.0	--	--	--
6	132,480	913.4	--	--	--
Mean	220,020	1517.0	--	--	--
<u>1000°C</u>					
7	--	--	--	--	--
8	173,980	1199.5	--	--	--
9	52,150	359.6	--	--	--
Mean	113,065	779.6	--	--	--
<u>25°C After 1000°C/100 hr Exposure</u>					
10	177,780	1225.7	26.7	184.1	0.26
11	36,360**	250.7	--	--	--
12	137,370	947.1	13.9	95.7	0.28
Mean	117,170	807.8	20.3	139.9	0.27

**Sample contained large open pore at surface.

TABLE X

THERMOPHYSICAL CHARACTERIZATION DATA FOR MULLITE AND ALUMINA SPECIMENS

BILLET DESCRIPTION	RETAINED TETRAGONAL PHASE V/O OF TOTAL	THERMAL CONDUCTIVITY - CAL/SEC °C CM (THERMAL DIFFUSIVITY - CM ² /SEC)			LINEAR COEFFICIENT OF EXPANSION $^{\circ}\text{C}^{-1} \times 10^6$ (RT - 700 °C)
		110 °C	700 °C	1250 °C	
MULLITE	N/A				5.0
MULLITE + 10 V/O ZrO ₂	5.6				5.8
MULLITE + 10 V/O (Zr _{0.5} Hf _{0.5} O ₂)	2.0	0.0085 (0.0127)	0.0065 (0.0078)	0.0050 (0.0069)	5.0
ALUMINA	N/A				8.1
ALUMINA + 15 V/O ZrO ₂	5.9				8.0
ALUMINA + 15 V/O (Zr _{0.5} Hf _{0.5} O ₂)	1.5	0.0362 (0.0417)	0.0136 (0.0120)	0.0126 (0.0101)	7.8

FIGURE 1

THE ZIRCONIA-HAFNIA SYSTEM (AFTER RUH ET AL.)

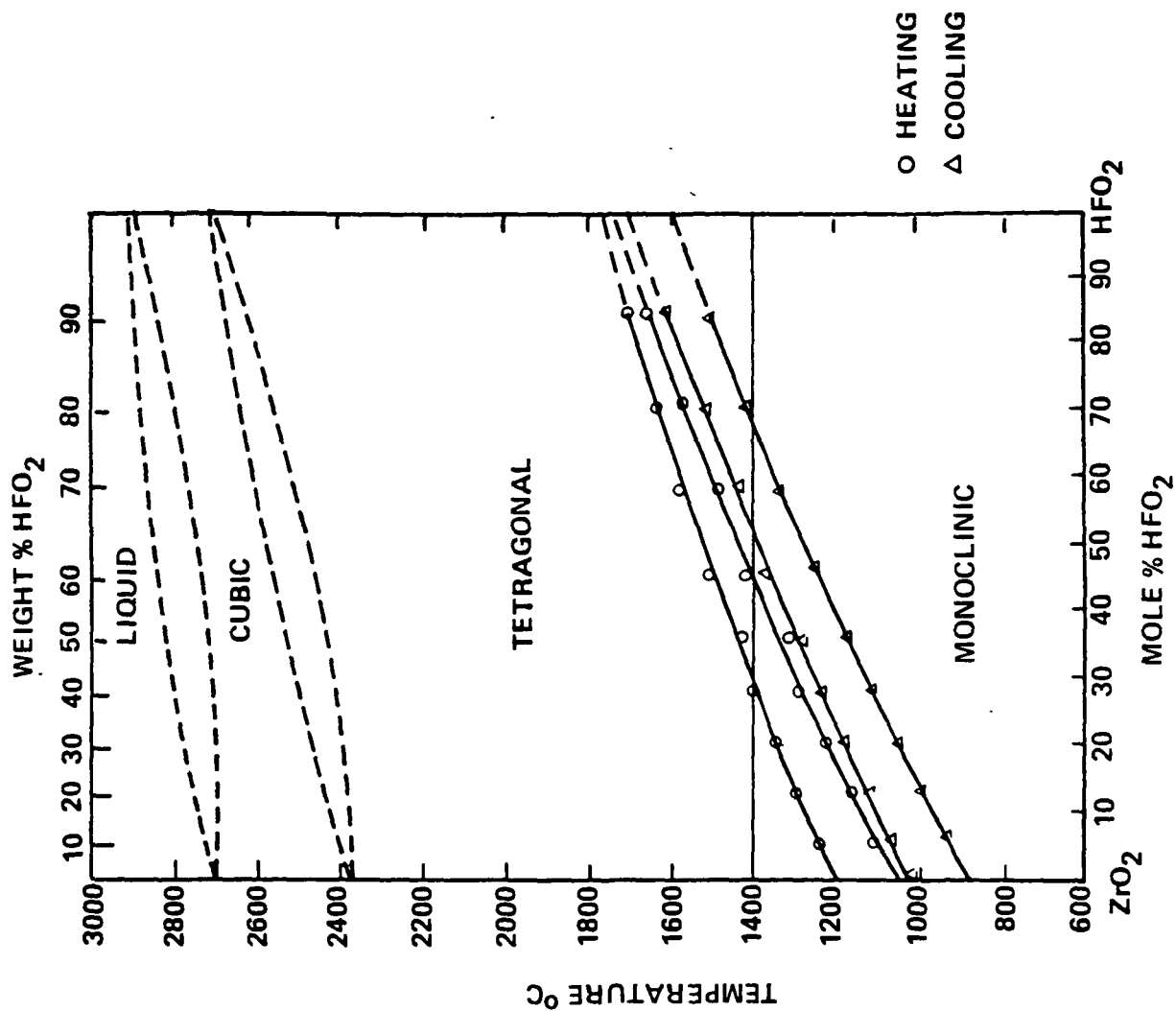
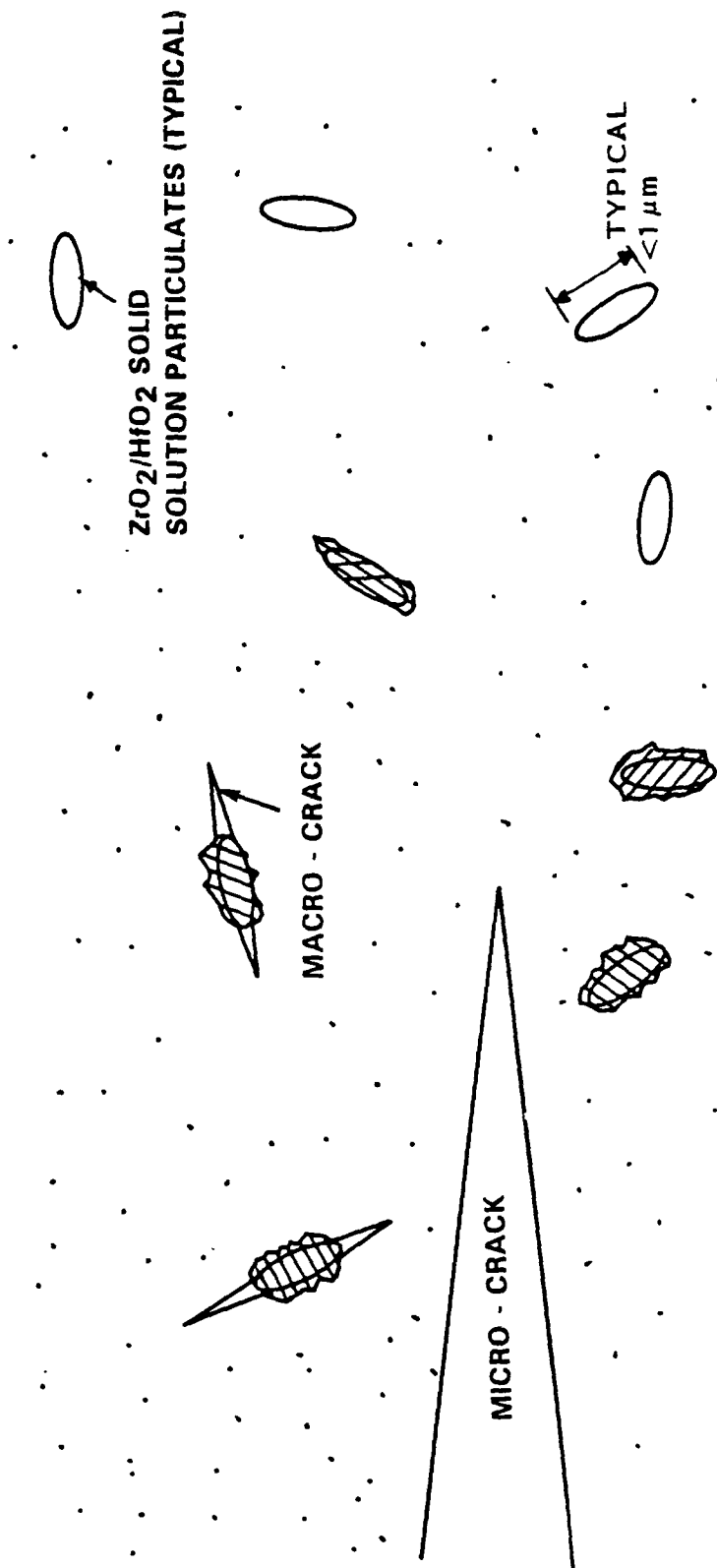


FIGURE 2

SCHEMATIC - TRANSFORMATION TOUGHENING



$\text{ZrO}_2/\text{HfO}_2$ SOLID SOLUTION TRANSFORMS IN STRESS FIELD OF CRACK TIP, COMPLEX STRESS AND STRAIN FIELD IMPEDES CRACK PROPAGATION AND ENHANCES K_{IC}

TETRAAGONAL \rightarrow MONOCLINIC, + ΔV

FIGURE 3

PREPARATION OF 1:1 ZrO₂ - HfO₂ POWDER MIXTURE BY SOL-GEL

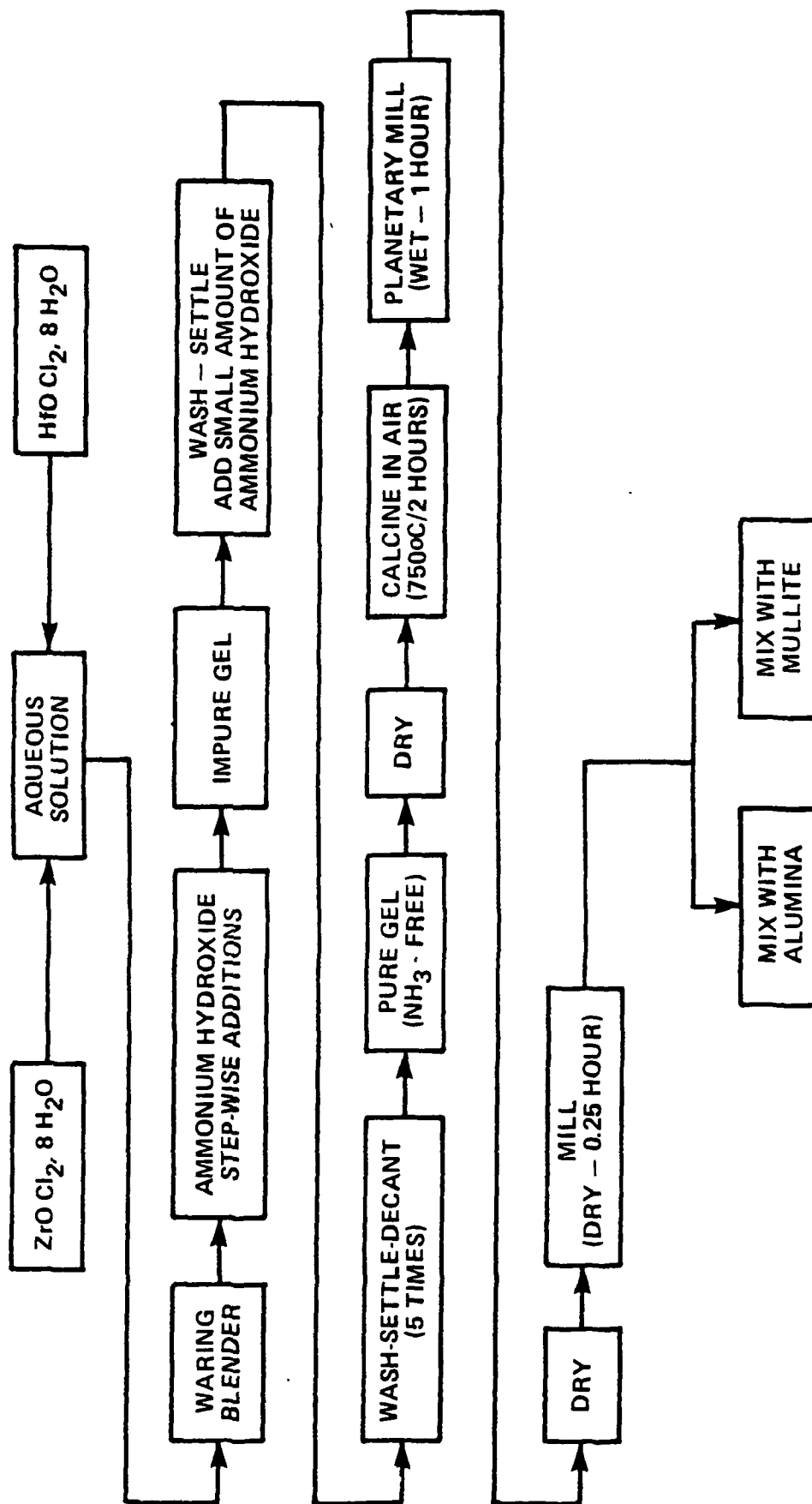
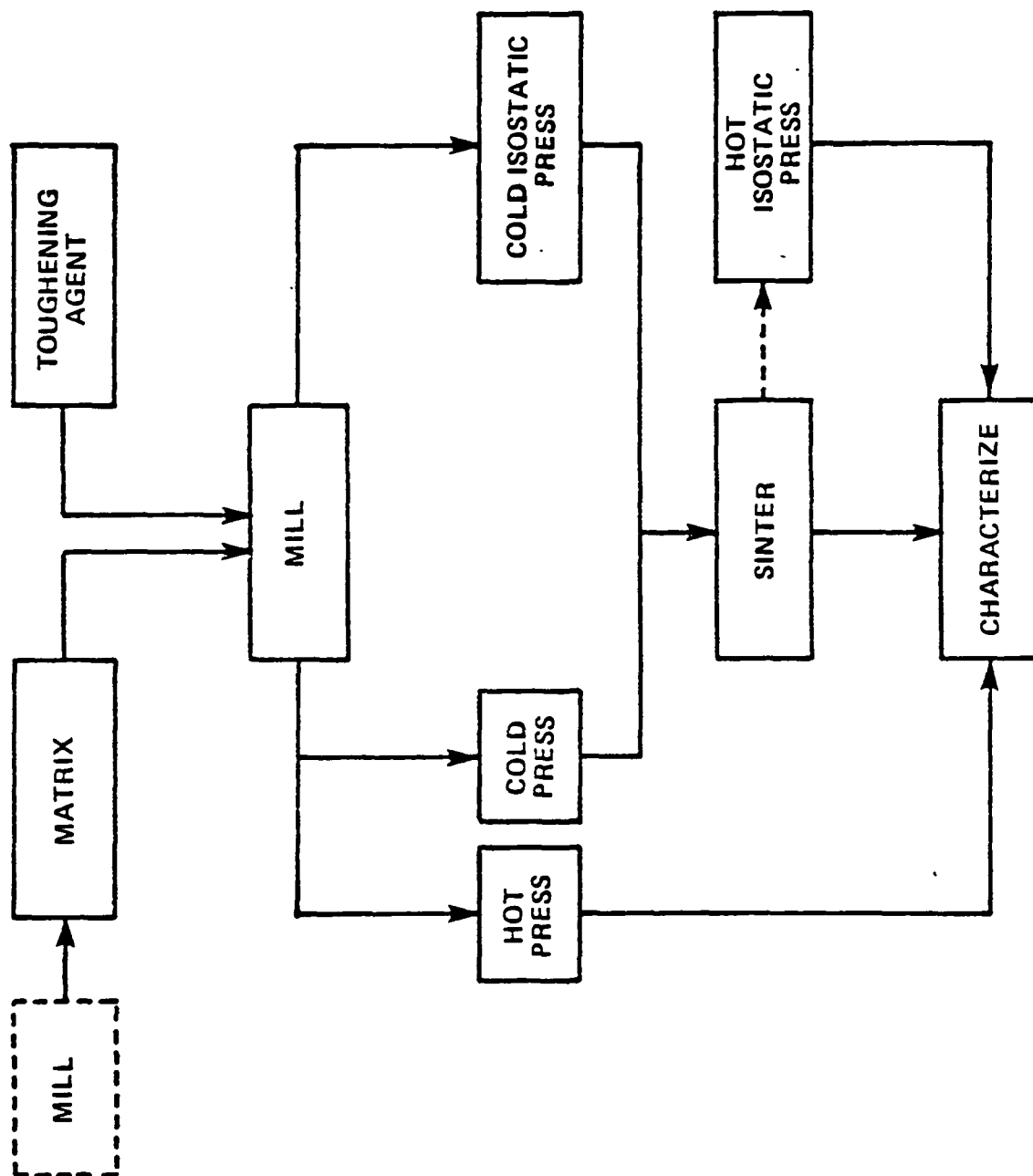
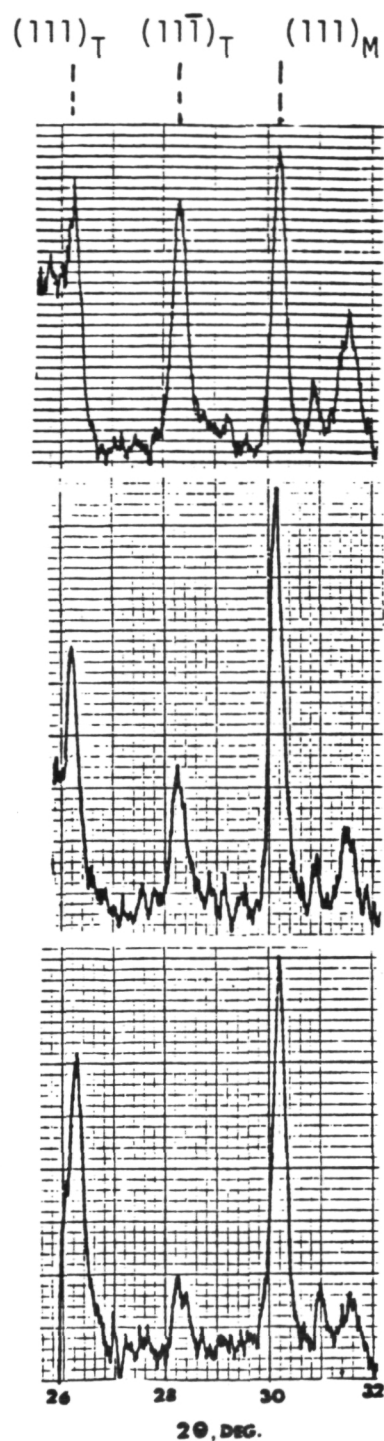


FIGURE 4

SCHEMATIC FABRICATING PROCESSES





ADDITIVE	RETAINED TETRAGONAL PHASE AS FRACTION OF ADDITIVE
1:1 $\text{ZrO}_2 - \text{HfO}_2$ Spec. No. T111684	0.40
2:1 $\text{ZrO}_2 - \text{HfO}_2$ Spec. No. TT120784A	0.66
All ZrO_2 Spec. No. TT20784B	0.78

FIGURE 5 X-RAY DIFFRACTION PATTERNS FOR SPECIMENS
SHOWING FRACTION OF RETAINED TETRAGONAL

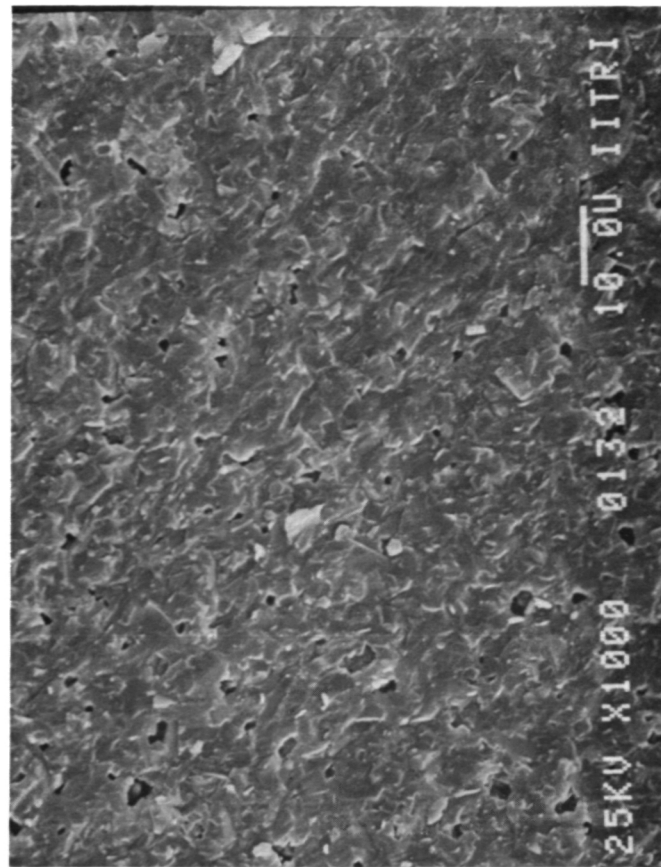
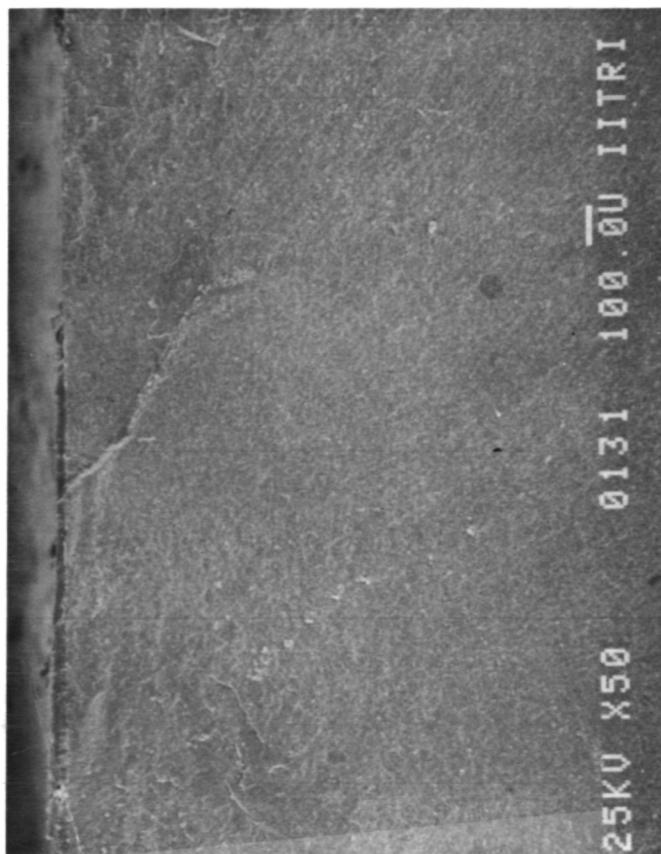


FIGURE 6 FRACTURE SURFACE MULLITE ROOM TEMPERATURE FLEXURE

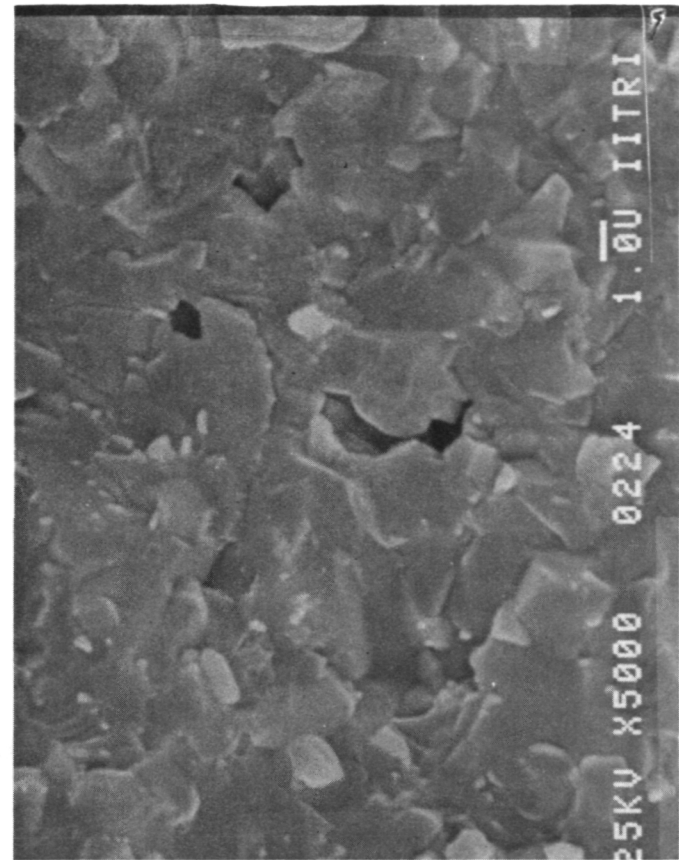
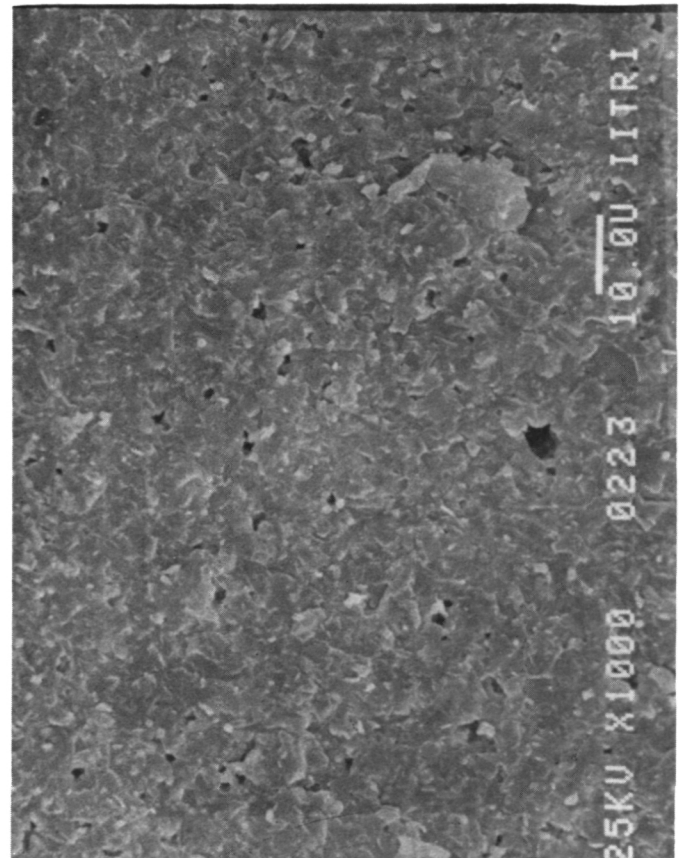
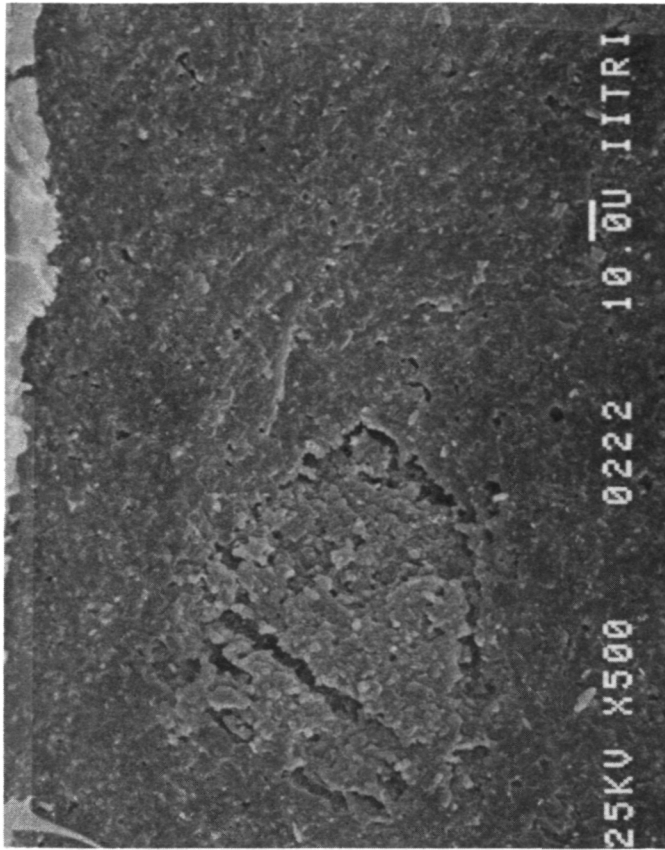
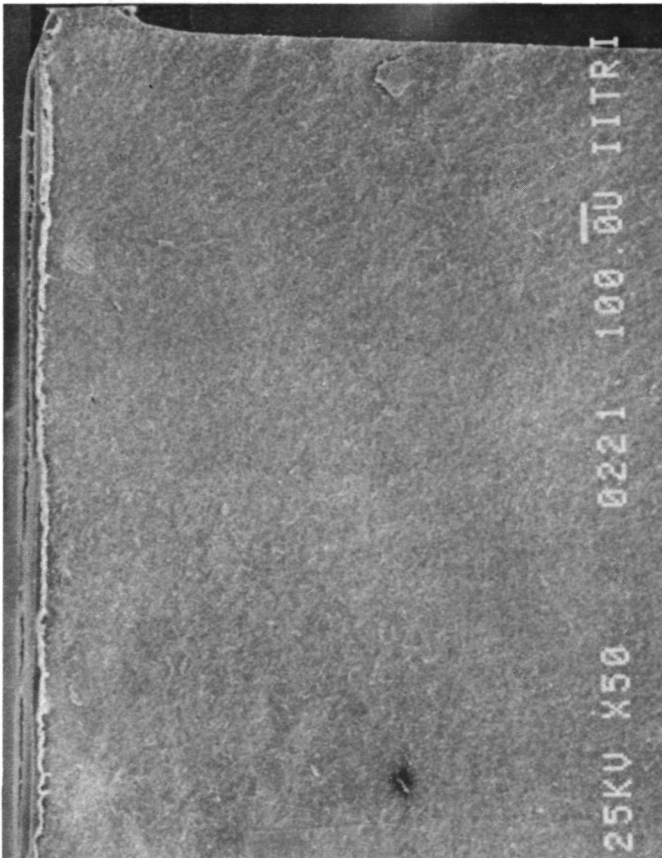


FIGURE 7 FRACTURE SURFACE - MULLITE 10 v/o ZrO2 ROOM TEMPERATURE FLEXURE

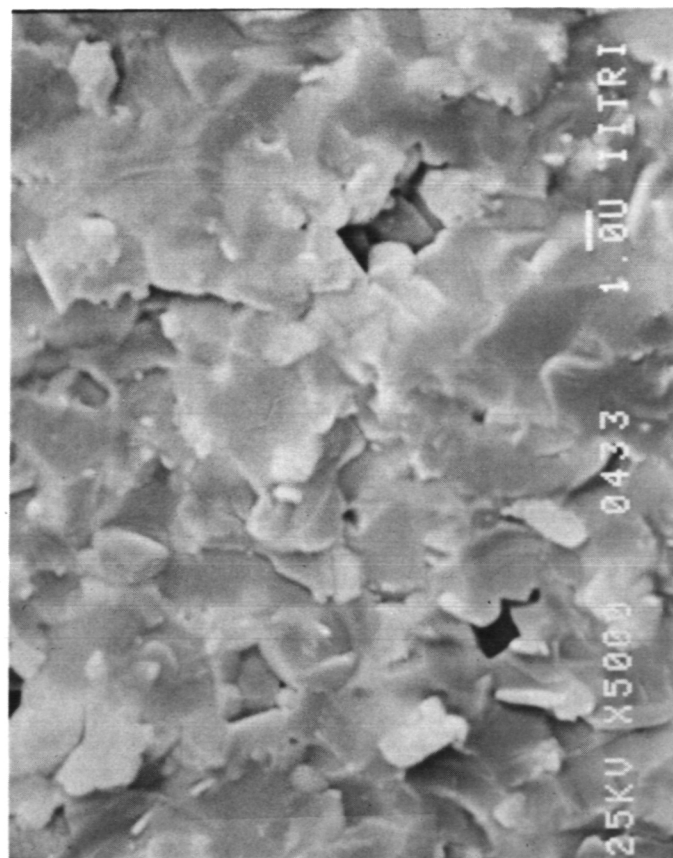
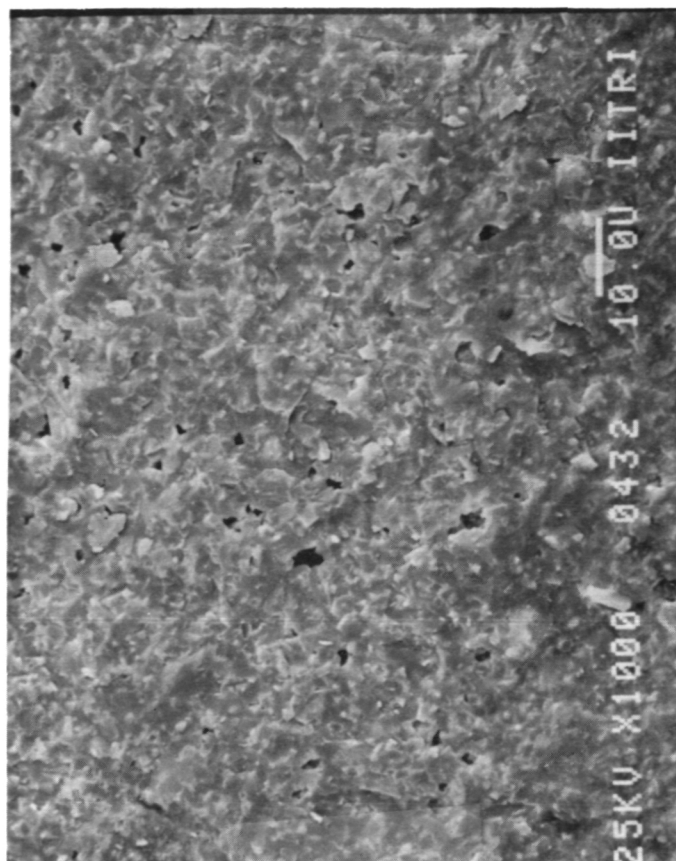
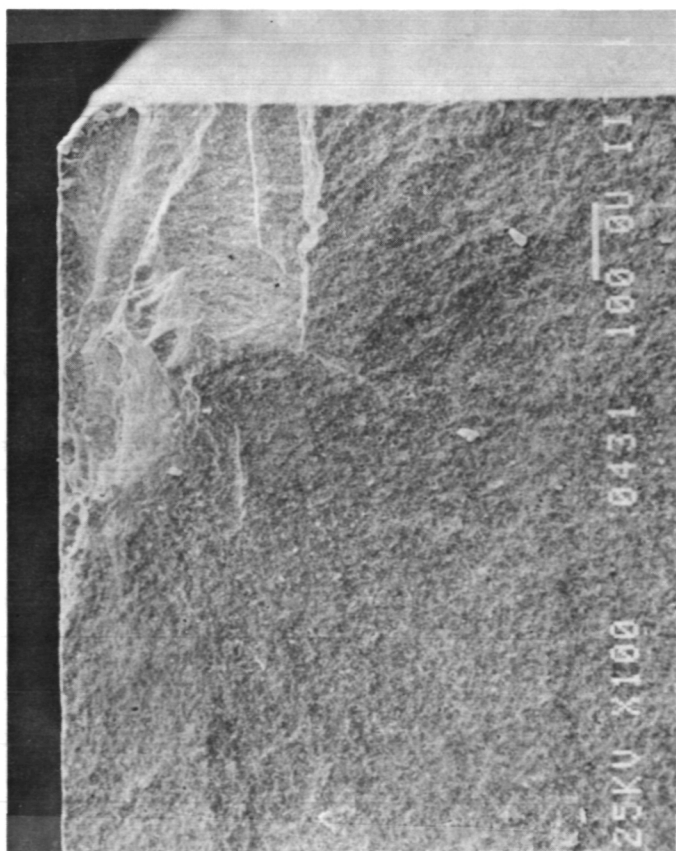


FIGURE 8 FRACTURE SURFACE MULLITE 10 v/o 2:1 ZrO2 HF02
ROOM TEMPERATURE FLEXURE

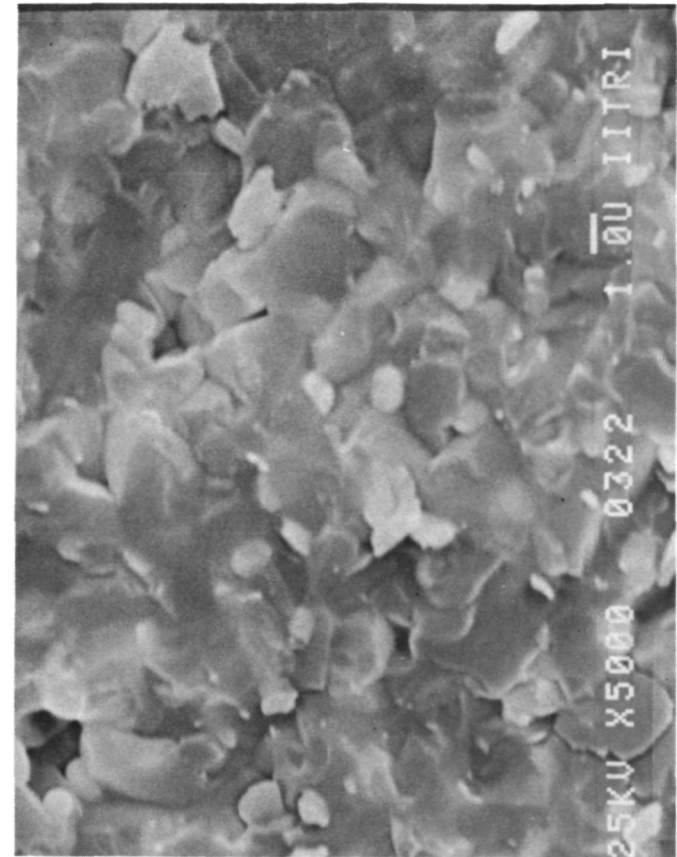
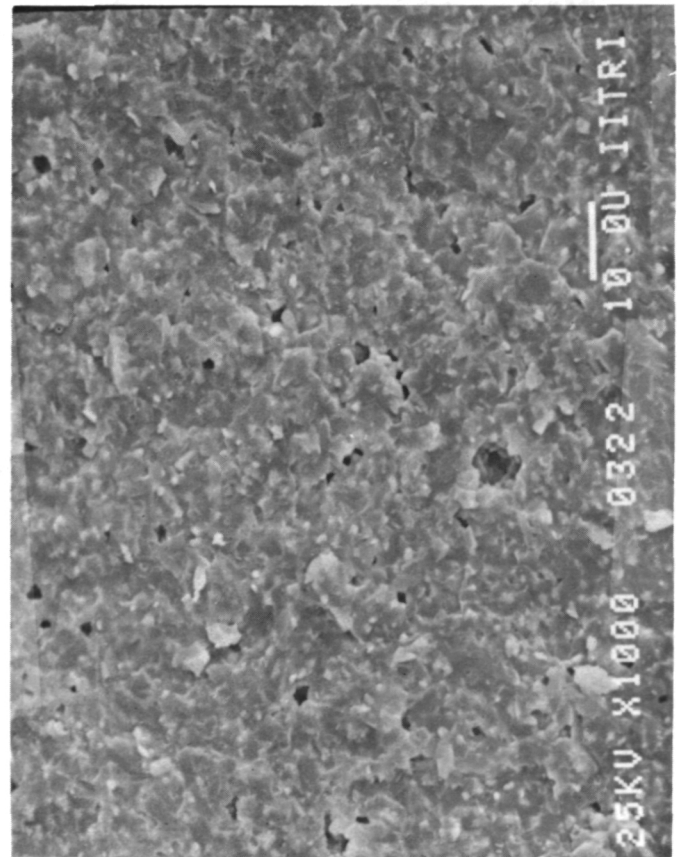
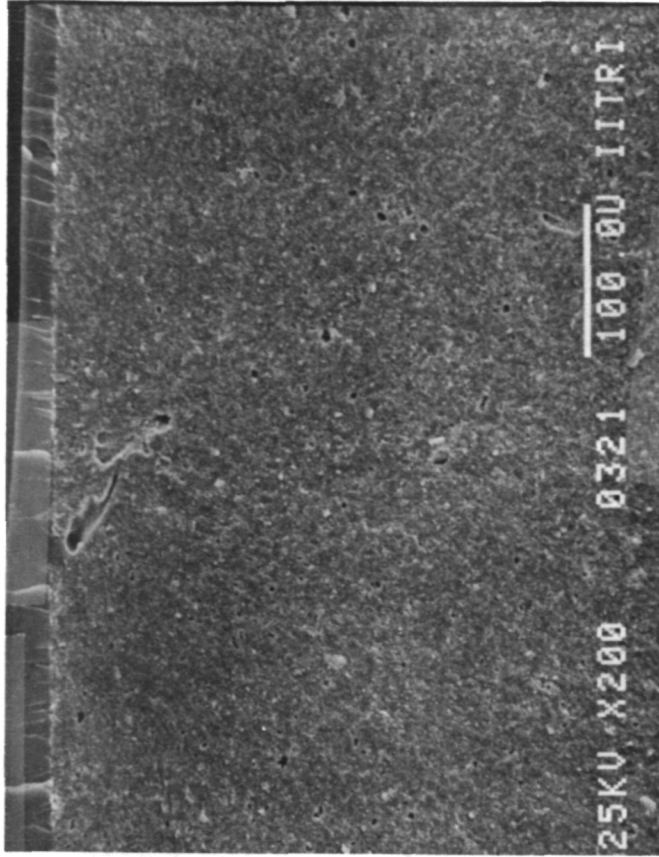
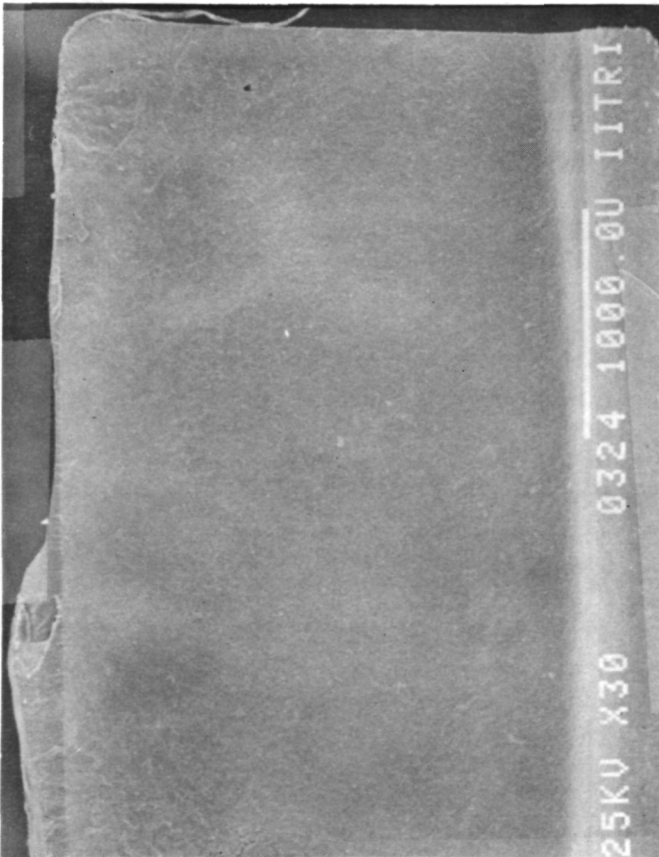
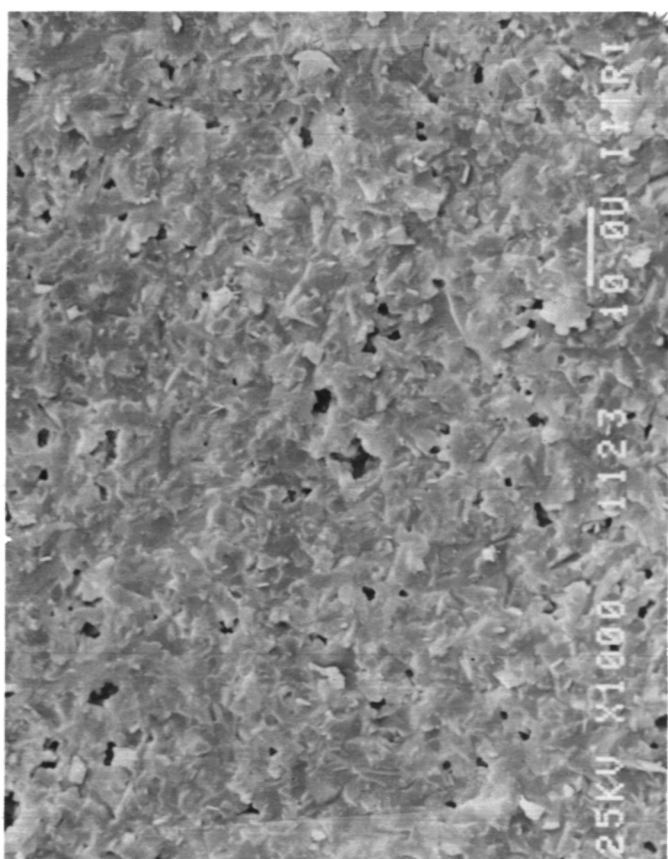
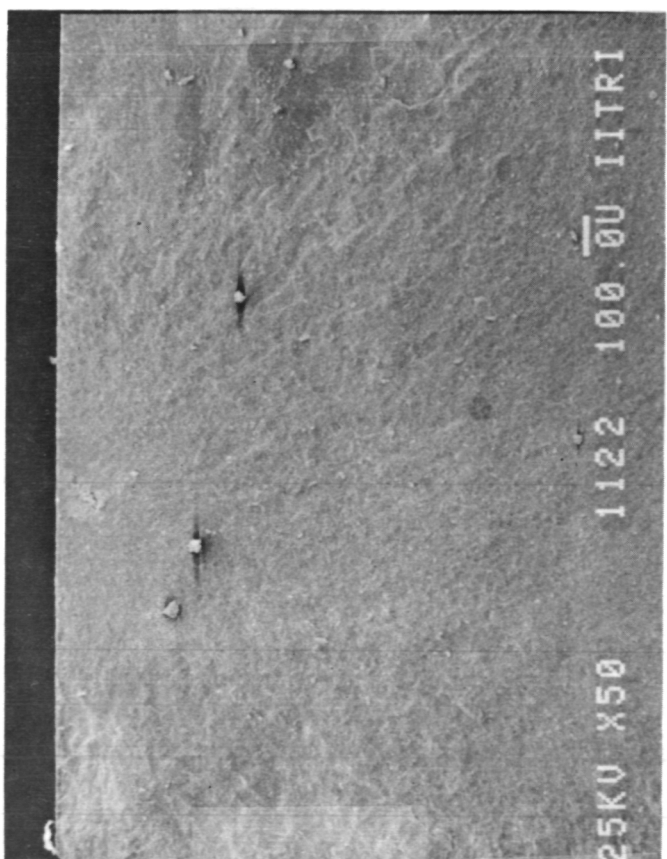
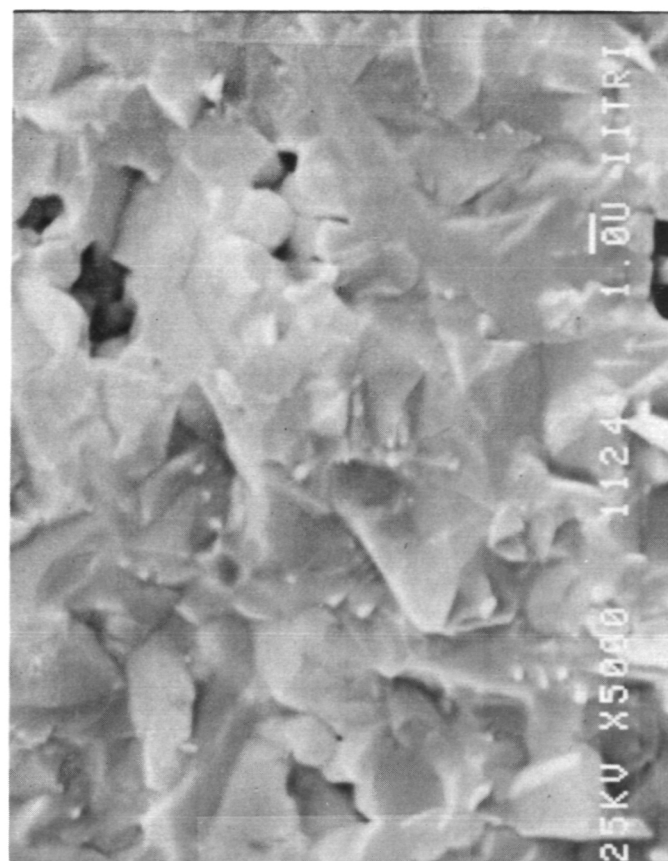
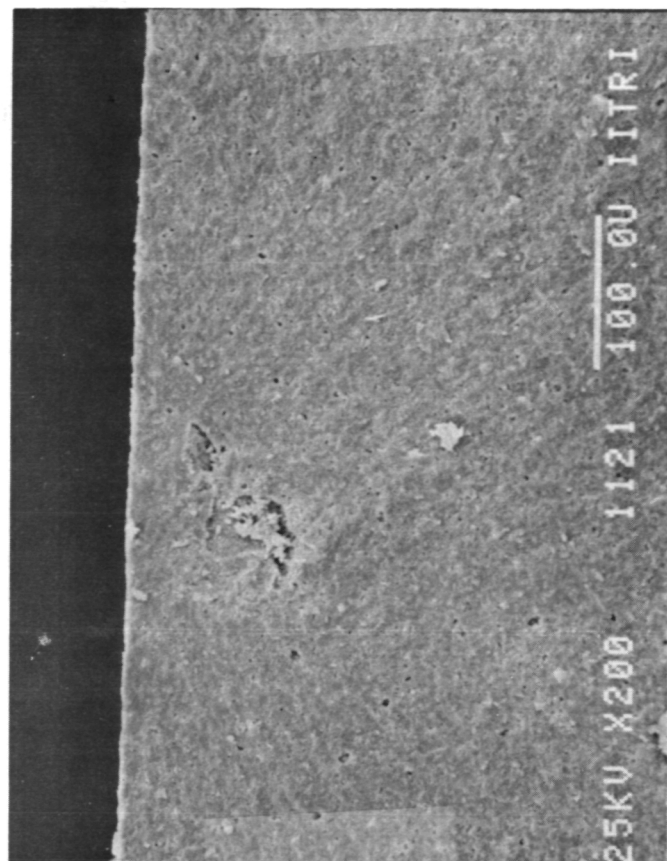


FIGURE 9 FRACTURE SURFACE MULLITE - 10 v/o 1:1 ZrO₂-HfO₂
ROOM TEMPERATURE FLEXURE



MULLITE 1000 C FLEXURE

FIGURE 10 FRACTURE SURFACE

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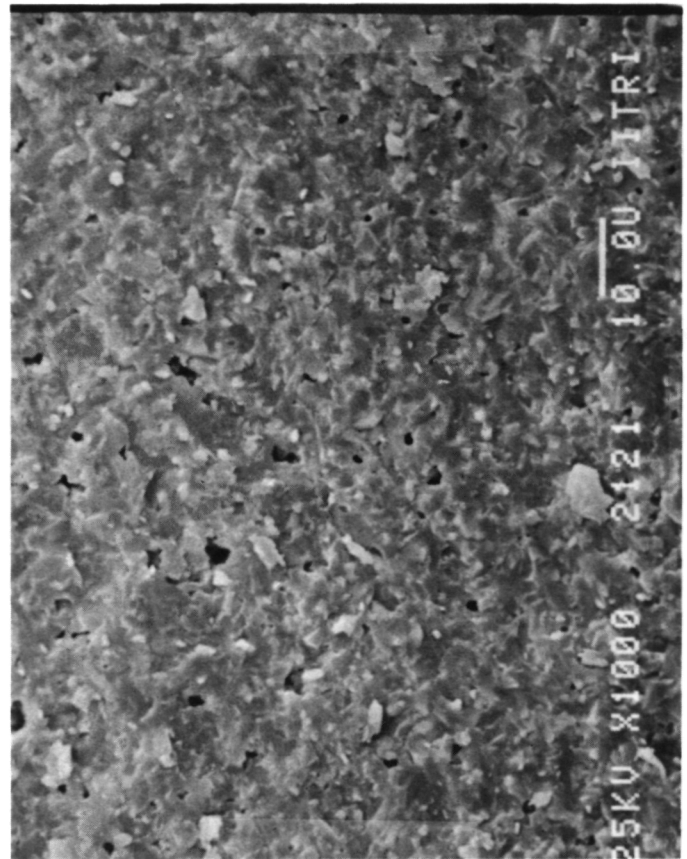
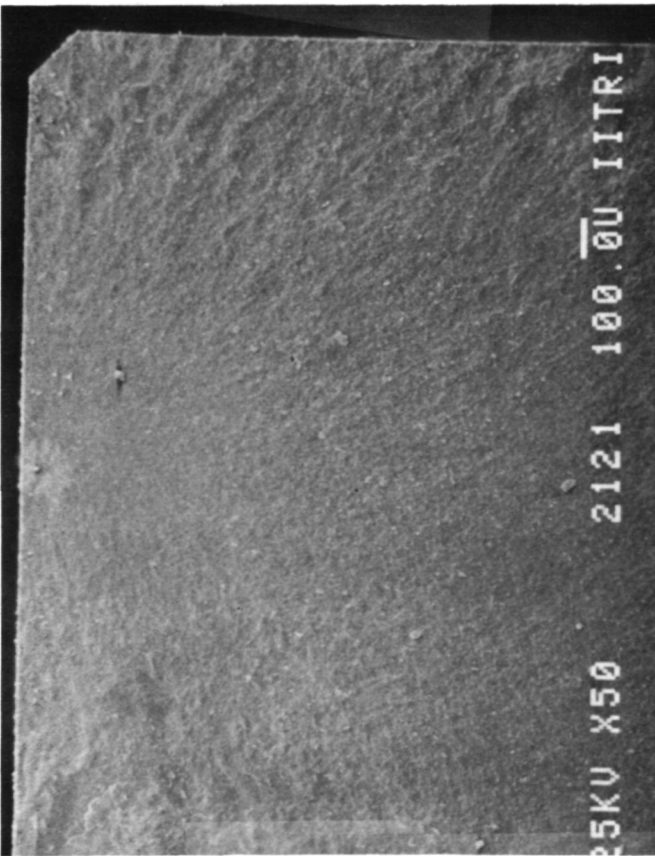
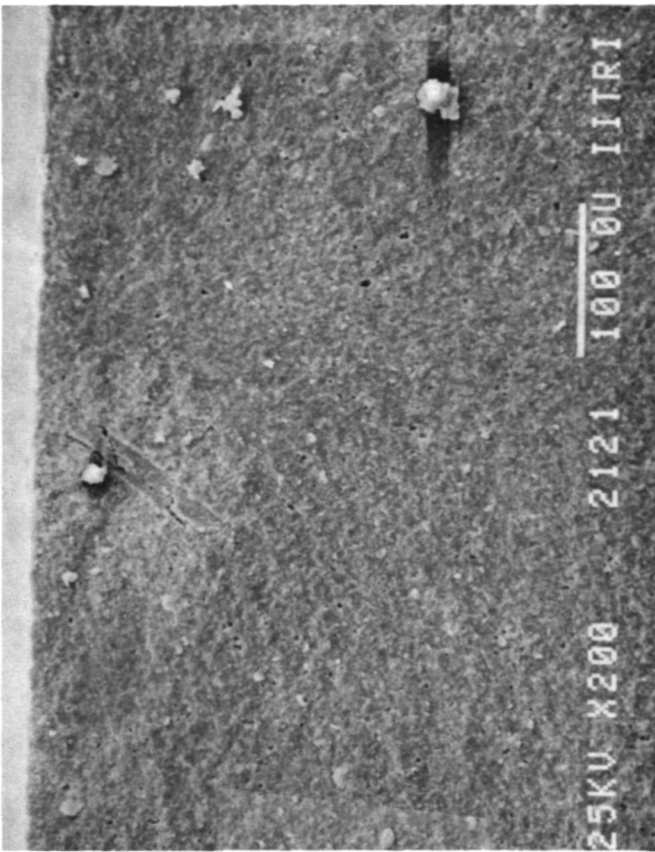


FIGURE 11 FRACTURE SURFACE MULLITE - 10 v/o ZrO₂ 1000 C FLEXURE

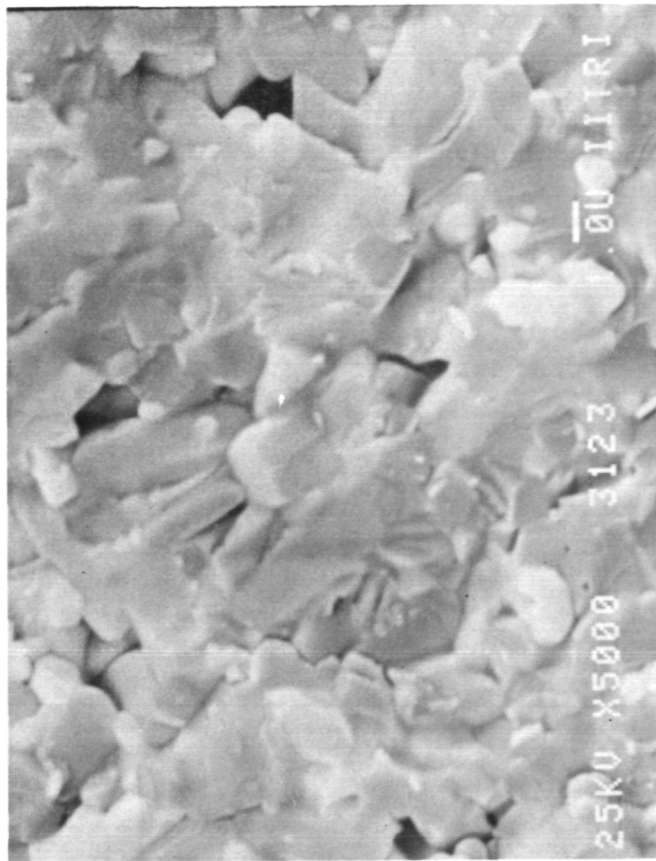
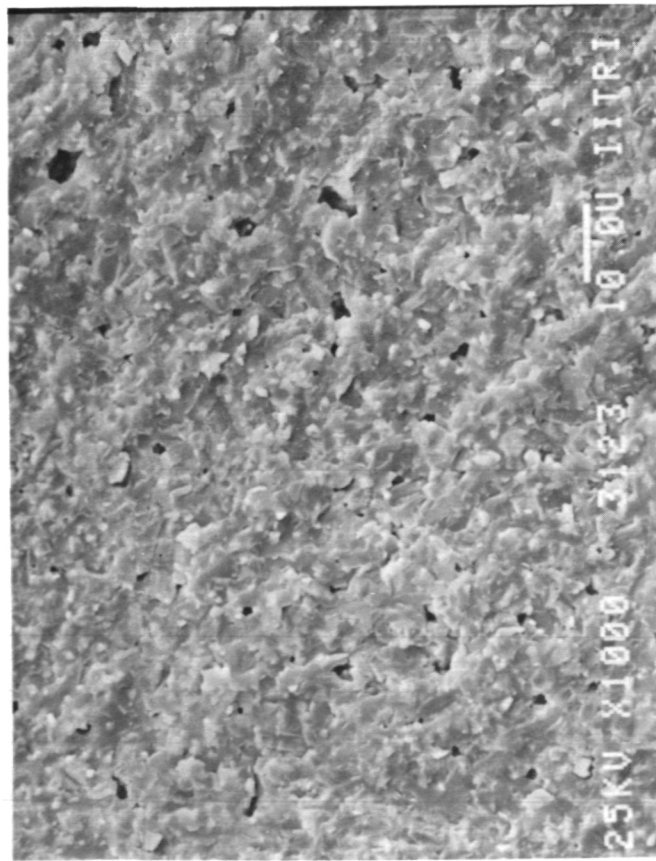
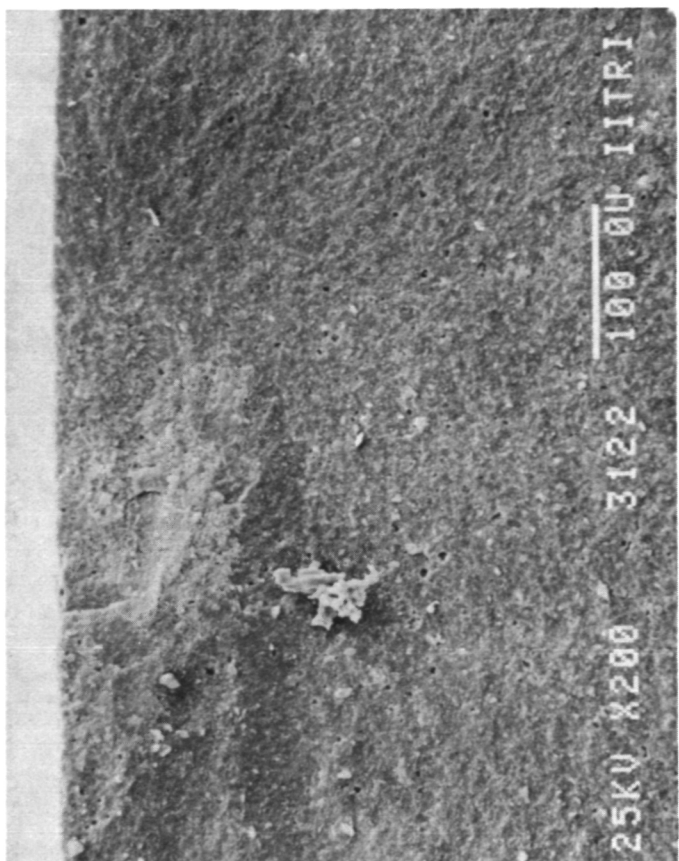
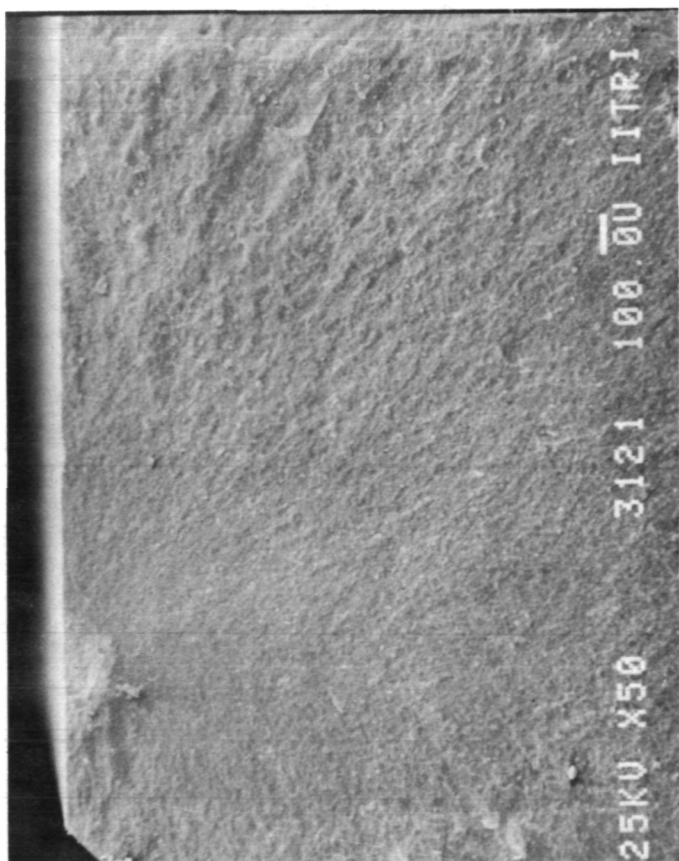


FIGURE 12 FRACTURE SURFACE
1000 C FLEXURE

MULLITE 10 v/o 1:1 ZrO2 HF02

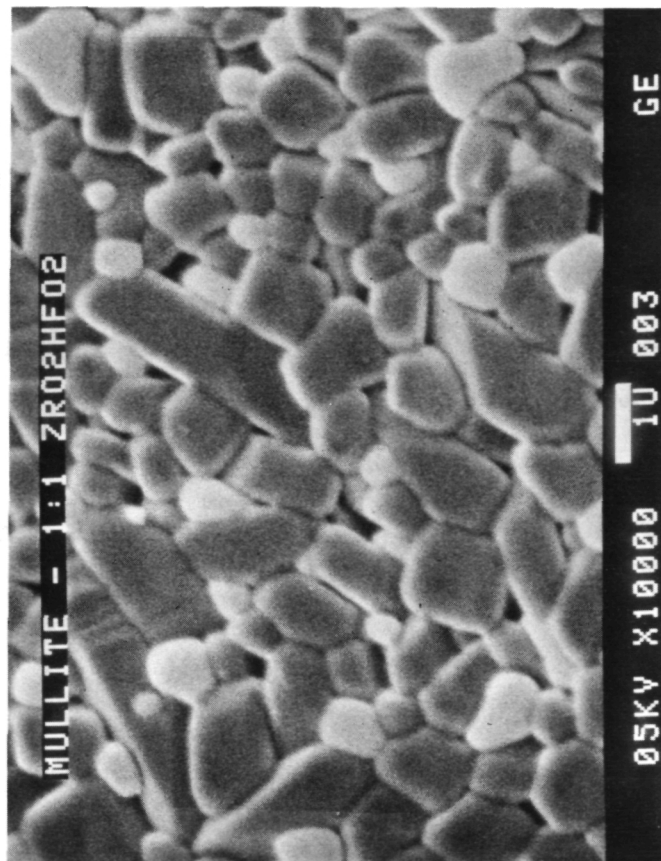
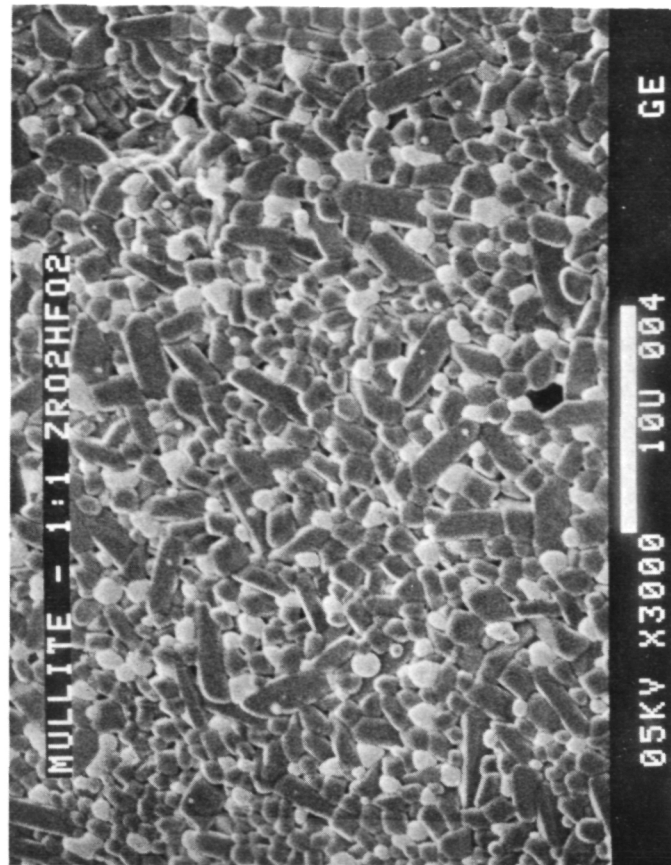
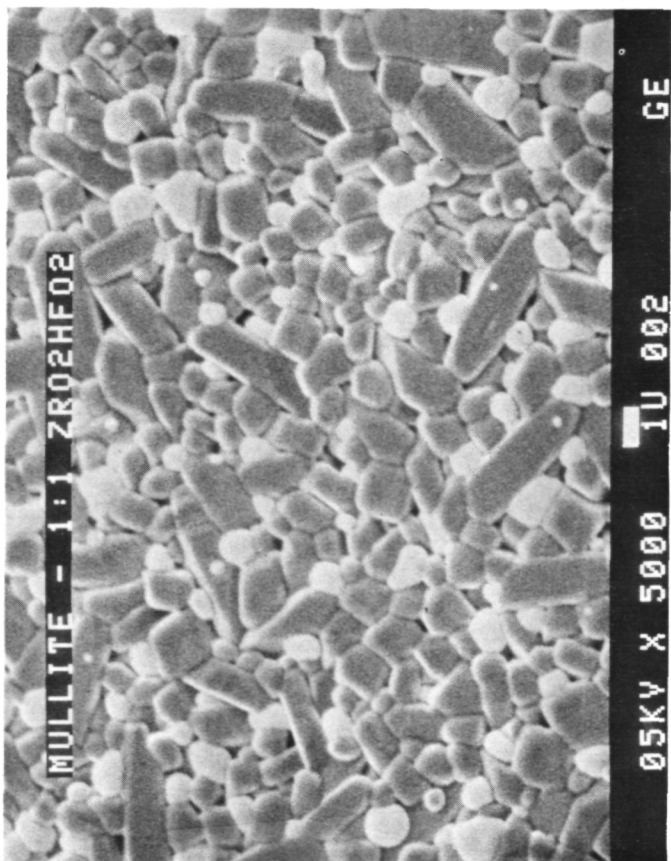
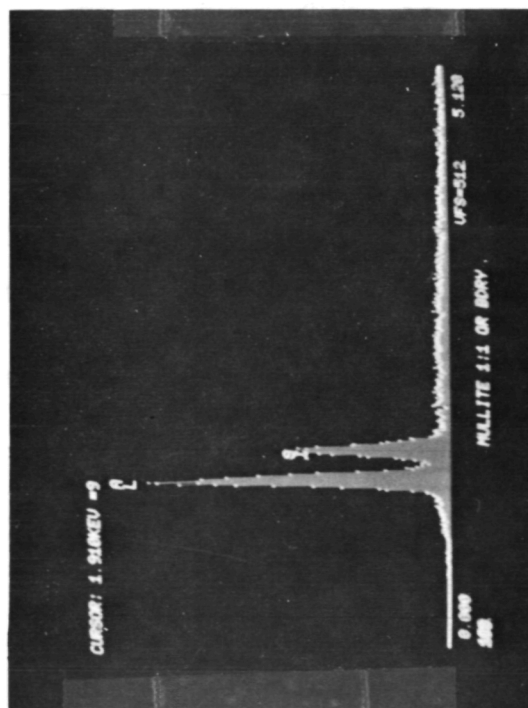
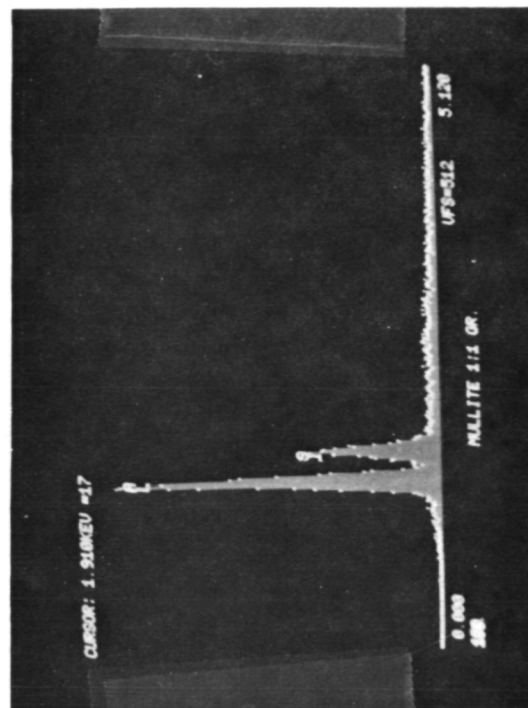


FIGURE 13 MICROSTRUCTURE MULLITE 10 v/o ZrO2 HF02
POLISHED AND THERMALLY ETCHED SURFACE

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(A)



(B)

FIGURE 14 COMPOSITION OF A MULLITE-ZrO₂/HfO₂ GRAIN BOUNDARY (A) AND A MULLITE GRAIN (B) IN MULLITE-10 v/o 1:1 ZrO₂-HfO₂

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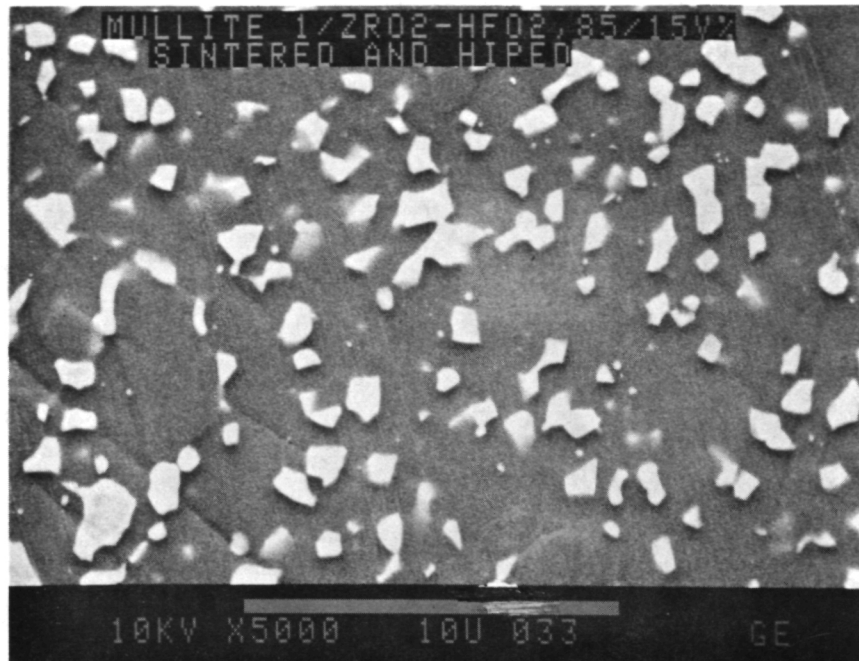


FIGURE 15 MICROSTRUCTURE OF MULLITE NO. 1A/ZrO₂-HfO₂, 85/15 V% (TT052185-1), SINTERED AND HIPed



FIGURE 16 MICROSTRUCTURE OF MULLITE NO. 1A/ZrO₂-HfO₂, 90/10 V% (TT05218502), SINTERED AND HIPed

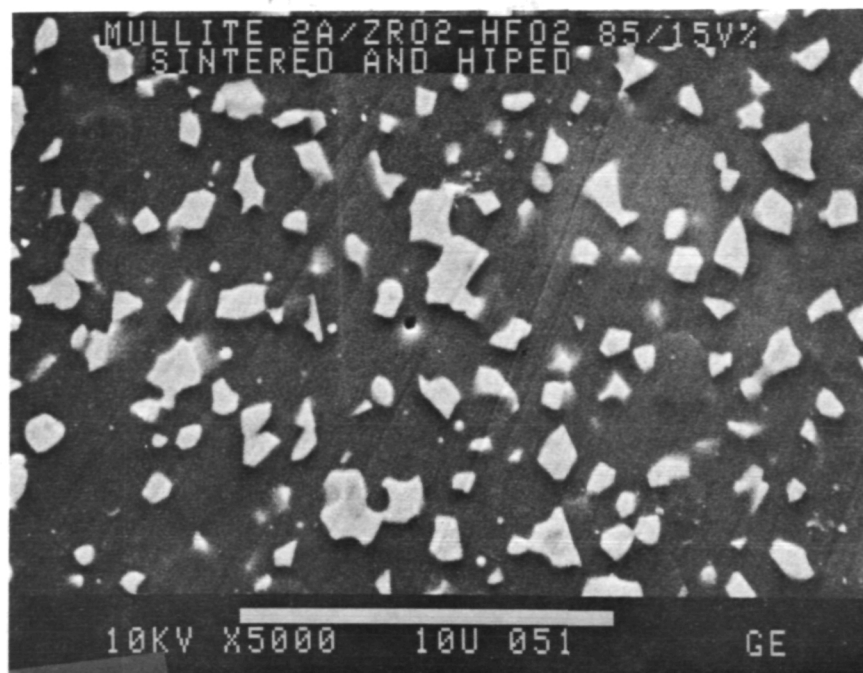


FIGURE 17 MICROSTRUCTURE OF MULLITE NO. 1A/ZrO₂-HfO₂, 85/15 V% (TT052185-3), SINTERED AND HIPed

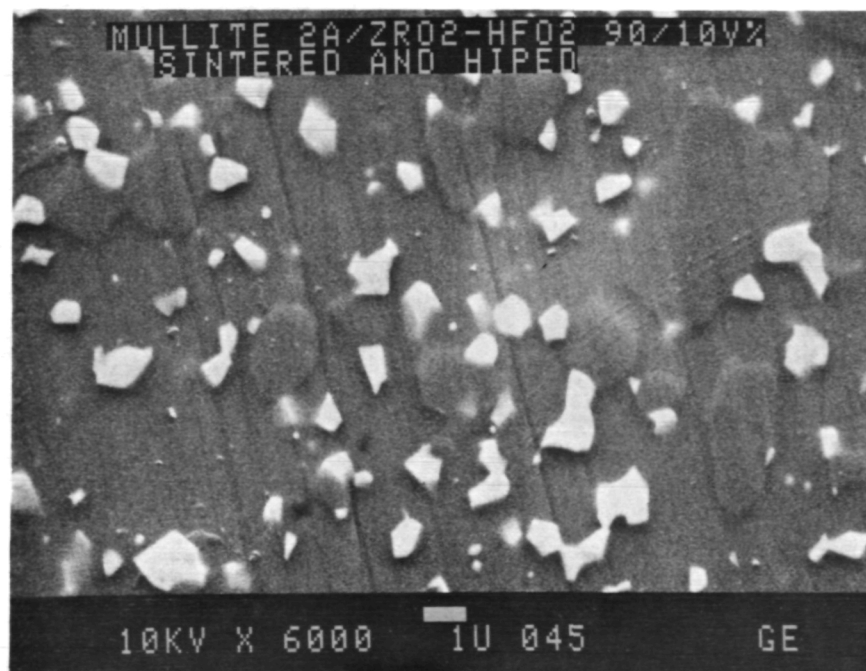


FIGURE 18 MICROSTRUCTURE OF MULLITE NO. 2A/ZrO₂-HfO₂, 90/10 V% (TT052185-4), SINTERED AND HIPed

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FIGURE 19 MICROSTRUCTURE OF MULLITE NO. 2A/ZrO₂-HfO₂, 90/10 V%
(TT061485), SINTERED

FIGURE 20

SINTERING STUDY 90 V/O MULLITE 10 ZrO.5Hf0.5O2

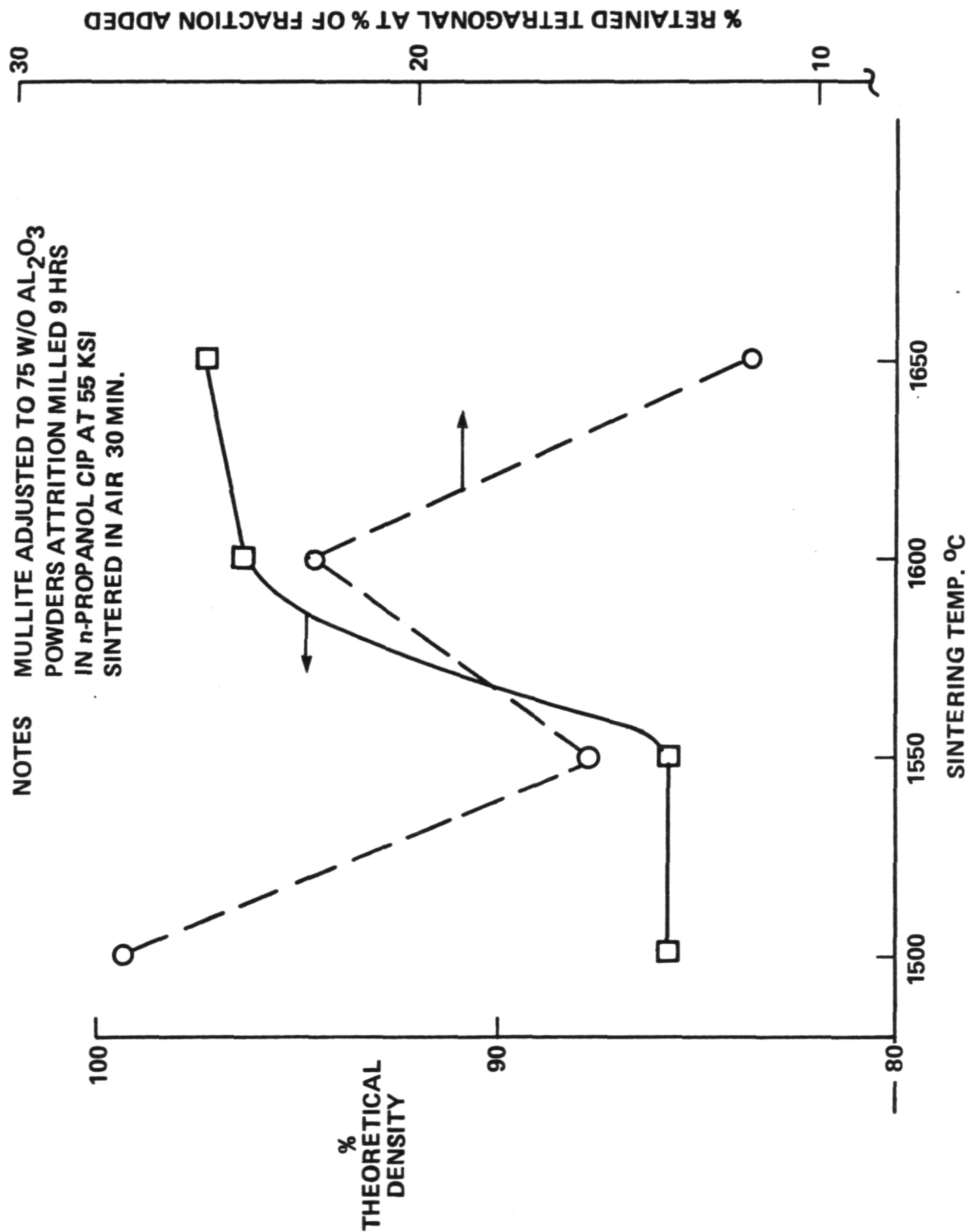
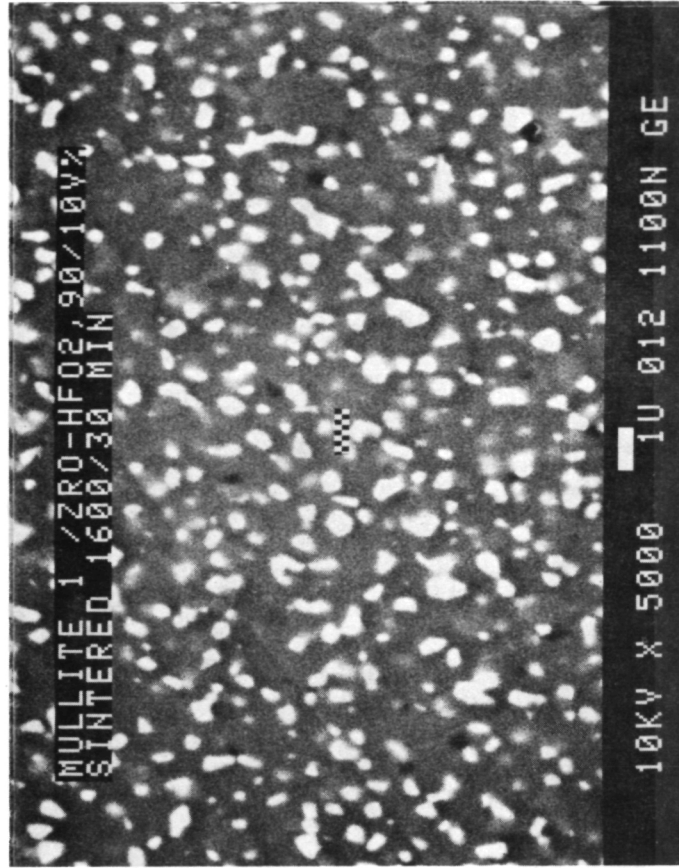
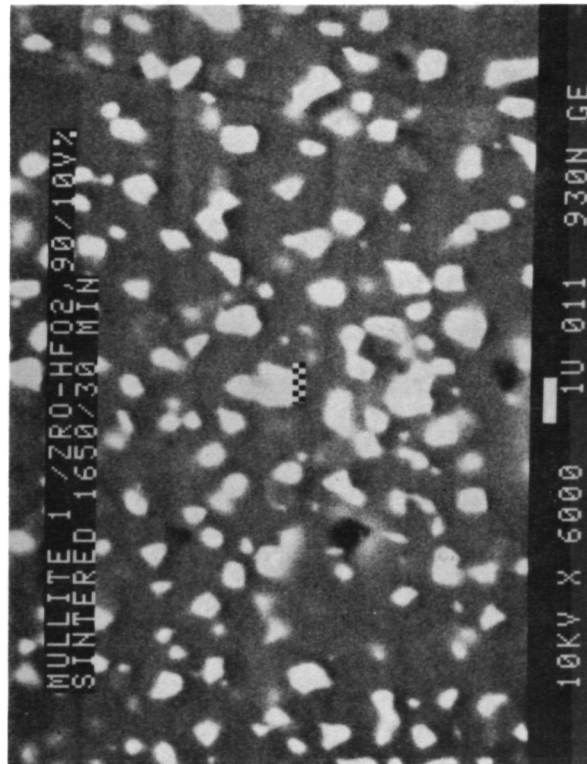


FIGURE 21

COMPARISON OF SECOND PHASE PARTICLE SIZE FOR TWO SINTERING SCHEDULE



B. 1600 C/30 MIN



A. 1650 C/30 MIN

APPENDIX I

Report No. IITRI-M06138-1

MECHANICAL PROPERTIES OF TOUGHENED MULLITE

General Electric Company
Space Systems Division
Valley Forge Space Center
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Philadelphia, Pennsylvania 19101

Attention: Dr. Solomon Musikant

Prepared by

Jane W. Adams

IIT Research Institute
10 West 35 Street
Chicago, Illinois 60616

11 November 1985

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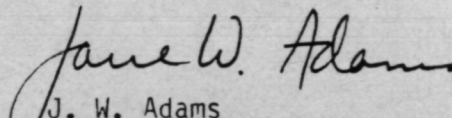
FOREWORD

This report contains the results of mechanical property evaluation of various toughened mullite compositions that General Electric is developing for DOE/NASA. The materials employ mullite as a matrix for a dispersed toughening phase of $\text{ZrO}_2/\text{HfO}_2$ solid solutions.

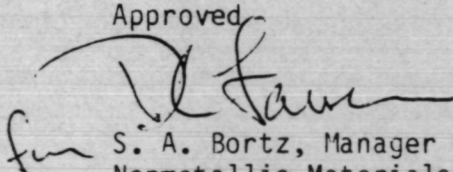
Flexure strength and fracture origin analysis, elastic modulus, and fracture toughness were evaluated for eleven developmental materials. Data were compared to transformation-toughened zirconia values where appropriate.

Respectfully submitted,

IIT RESEARCH INSTITUTE


J. W. Adams
Associate Engineer

Approved



S. A. Bortz, Manager
Nonmetallic Materials and Composites
Materials and Processing Technology

1. FLEXURAL STRENGTH

The flexural strength was determined in the quarter 4-point configuration on test samples that were of nominal dimensions 3 x 4 x 45 mm. The upper and lower spans were 20 and 40 mm, respectively, and the strain rate was $9.5 \times 10^{-5} \text{ sec}^{-1}$ (a crosshead speed of 0.5 mm/min). The sample and fixture dimensions conform to fixture configuration B in MIL-STD-1942 (MR), "Flexure Strength of High Performance Ceramics at Ambient Temperature."

The static elastic modulus was determined by measuring the outer fiber tensile strain during flexural strength testing. Resistance strain gages were used to measure deformation at 25°C. At elevated temperature a precision electromechanical instrument was employed, where deformation was recorded at three positions on the sample tensile face within the region of pure bending (i.e., within the upper span length). This was accomplished by extending SiC rods from an LVDT coil and core up through the furnace to the sample. In this manner, the outer fiber tensile strain was directly recorded, without the need to employ potentially inaccurate methods of subtracting out the fixture/load rod deformations.

The fast fracture bend strength results are presented in Tables 1 to 10 and Figure 1. The results of samples that were exposed for nominally 100 hr at 1000°C in static laboratory air prior to residual room temperature strength measurement are also included in the tables. Both toughened and non-toughened materials were tested. Generally the toughened materials retained ~75% of their room temperature strength in fast flexure testing at 800°C, although MULL 1:1 ZH, 10 v/o, and MULL 2A ZH, 10 v/o (a) retained only about 50%, while MULL 2A ZH, 10 v/o (b) retained 88%. Samples which were exposed at 1000°C/140 hr then tested at room temperature also had strengths ~75% of the unexposed room temperature values, with the exception of MULL 2A ZH, 10 v/o (a) which had a 25% increase in strength. In most cases the elastic moduli decreased as a function of temperature and exposure by a few percent, with MULL 2A ZH, 10 v/o (b) showing the least variation (although this material was not exposed at 1000°C).

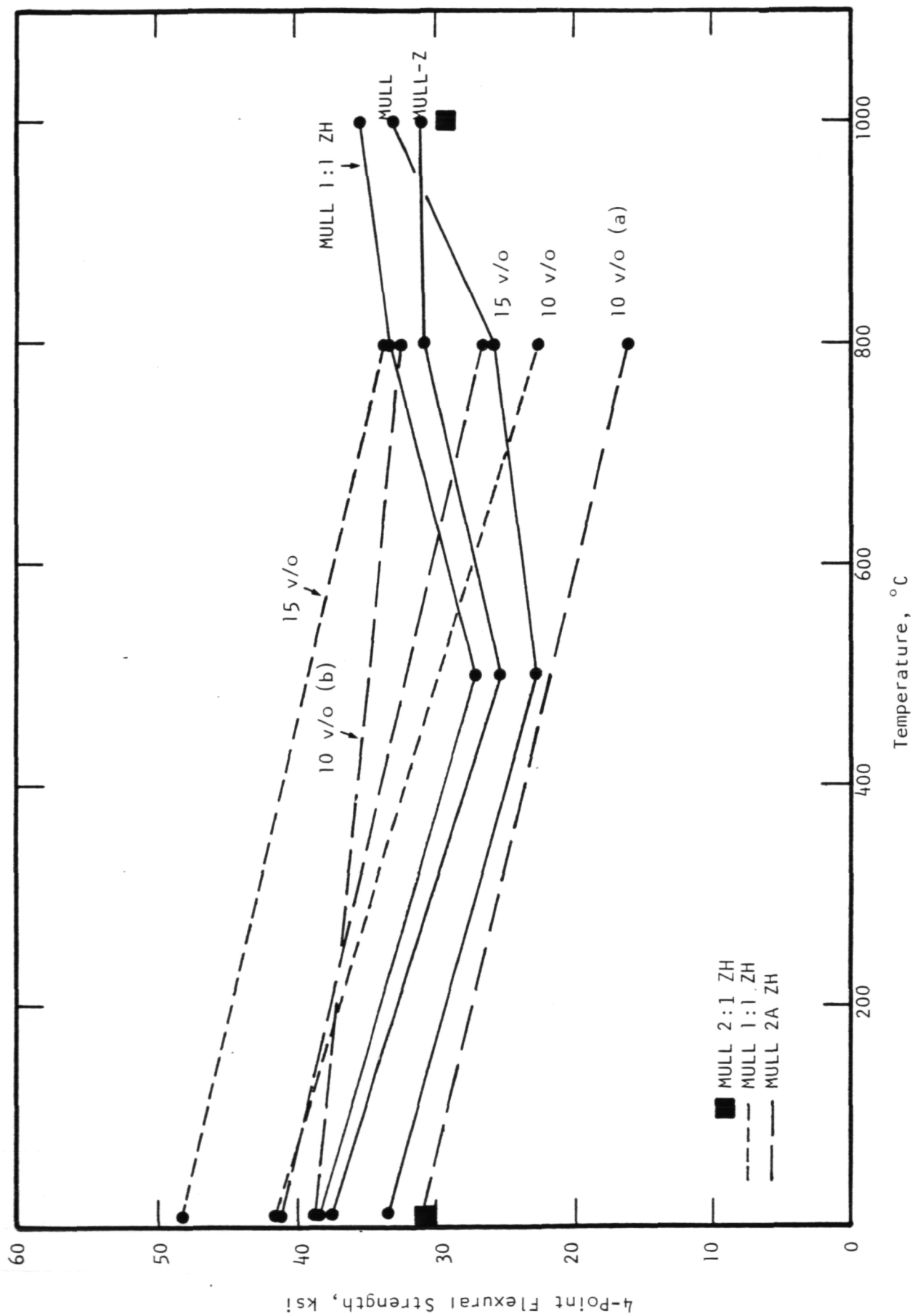


Figure 1. Flexural strength as a function of temperature.

All fracture surfaces were examined in a stereoscopic optical microscope, and selected samples in an SEM. Fracture origins are indicated in Tables 1 to 10. Most fracture origins were related to processing. Open or closed pores were small, singular, and generally round, either below the tensile surface, or exposed during test sample preparation by diamond grinding. "Processing defect" is a more general category, encompassing poorly sintered regions, pore clusters, or large irregularities in the overall structure, which may have appeared during cold pressing. Subsurface large grains in these materials were glassy in appearance. Examples of the various types of critical flaws are shown in Figure 2.

**TABLE 1. FLEXURE TEST RESULTS FOR MULL (IITRI SM1)
AT VARIOUS TEMPERATURES**

Sample Number	4-Point Flexure Strength		Failure Strain, %	Elastic Modulus	
	psi	MPa		10 ⁶ psi	GPa

a. Strength at Various Temperatures

<u>25°C</u>					
1	32,840	226.4	0.12	27.0	186.4
2	32,580	224.6	0.12	27.8	191.6
3	34,880	240.5	0.13	26.8	184.6
Mean	33,430	230.6	0.12	27.2	187.5
<u>500°C</u>					
4	24,350	167.9	--	--	--
5	23,030	158.8	0.07	32.5	223.8
6	21,550	148.6	0.06	36.7	253.3
Mean	22,980	158.4	0.07	34.6	238.6
<u>800°C</u>					
7	27,670	190.8	0.08	34.3	236.4
8	23,180	159.9	0.07	33.4	230.0
9	26,970	186.0	0.09	29.3	201.7
Mean	25,940	178.9	0.08	22.6	222.7
<u>1000°C</u>					
10	31,740	218.9	0.13	23.9	165.0
11	31,760	219.1	0.11	28.2	194.8
12	35,410	244.2	0.14	25.4	175.5
Mean	32,970	227.4	0.13	25.8	178.4

b. Fracture Origins

Sample Number	Critical Flaw Type					
	Open Pore	Closed Pore	Processing Defect	Subsurface Large Grain	Machining Flaw	Undeter- mined
1			•			
2	•					
3			•			
4	•					
5	•					
6						•
7		•				
8						•
9		•				
10		•				
11	•					
12			•			

TABLE 2. FLEXURE TEST RESULTS FOR MULL-Z (IITRI SM2)
AT VARIOUS TEMPERATURES

Sample Number	4-Point Flexure Strength		Failure Strain, %	Elastic Modulus	
	psi	MPa		10 ⁶ psi	GPa

a. Strength at Various Temperatures

<u>25°C</u>					
1	29,980	206.8	0.11	27.1	187.2
2	46,390	319.9	0.17	27.7	191.3
3	36,550	252.0	0.13	27.9	192.1
Mean	37,640	259.6	0.14	27.6	190.2
<u>500°C</u>					
4	24,040	165.8	0.06	37.9	261.3
5	22,280	153.6	0.06	35.3	243.5
6	29,210	201.4	0.09	34.1	234.9
Mean	25,180	173.6	0.07	35.8	246.6
<u>800°C</u>					
7	32,000	220.7	0.13	28.2	194.2
8	25,240	174.1	0.09	27.3	188.5
9	33,990	234.4	0.10	33.1	228.5
Mean	30,410	209.7	0.11	29.5	203.7
<u>1000°C</u>					
10	32,220	222.2	0.13	25.3	174.3
11	24,880	171.6	0.10	23.7	163.7
12	36,530	251.9	0.17	21.2	145.9
Mean	31,210	215.2	0.13	23.4	161.3

b. Fracture Origins

Sample Number	Critical Flaw Type					
	Open Pore	Closed Pore	Processing Defect	Subsurface Large Grain	Machining Flaw	Undeter- mined
1		•				
2			•			
3		•				
4			•			
5	•					
6	•					
7		•				
8		•				
9			•			
10	•					
11		•				
12				•		

TABLE 3. FLEXURE TEST RESULTS FOR MULL 1:1 ZH (IITRI SM3)
AT VARIOUS TEMPERATURES

Sample Number	4-Point Flexure Strength		Failure Strain, %	Elastic Modulus	
	psi	MPa		10 ⁶ psi	GPa

a. Strength at Various Temperatures

<u>25°C</u>					
1	37,160	256.3	0.13	27.7	191.0
2	41,070	283.2	0.15	27.2	187.4
3	36,210	249.7	0.13	28.0	193.2
Mean	38,150	263.1	0.14	27.6	190.5
<u>500°C</u>					
4	27,540	189.9	0.08	34.9	240.8
5	28,030	193.3	0.08	37.4	257.7
6	25,410	175.3	0.10	26.4	181.8
Mean	26,990	186.2	0.09	32.9	226.8
<u>800°C</u>					
7	34,130	235.4	0.13	26.4	182.1
8	32,300	222.7	0.12	27.0	186.0
9	33,440	230.6	0.12	28.0	193.1
Mean	33,290	229.6	0.12	27.1	187.1
<u>1000°C</u>					
10	32,410	223.5	0.15	21.4	147.7
11	35,830	247.1	0.20	18.3	126.0
12	38,130	262.9	0.17	22.8	157.1
Mean	35,460	244.5	0.17	20.8	143.6

b. Fracture Origins

Sample Number	Critical Flaw Type					
	Open Pore	Closed Pore	Processing Defect	Subsurface Large Grain	Machining Flaw	Undeter- mined
1						
2		•		•		
3		•				
4			•			
5			•			
6			•			
7		•				
8		•				
9	•					
10		•				
11		•				
12						•

TABLE 4. FLEXURE TEST RESULTS FOR MULL 2:1 ZH (IITRI SM4)

Sample Number	4-Point Flexure Strength		Failure Strain, %	Elastic Modulus	
	psi	MPa		10 ⁶ psi	GPa

a. Strength at Various Temperatures25°C

1	33,700	232.4	0.12	28.5	196.7
2	22,410	154.5	0.08	27.7	191.3
3	35,330	243.6	0.12	28.4	195.6
Mean	30,480	210.2	0.11	28.2	194.5

500°C

4	No material tested at 500°C				
5					
6					
Mean					

800°C

7	No material tested at 800°C				
8					
9					
Mean					

1000°C

10	29,080	200.5	0.17	17.0	117.5
11	33,050	227.9	0.16	19.9	137.3
12	25,710	177.3	0.13	19.8	136.5
Mean	29,280	201.9	0.15	18.9	130.4

b. Fracture Origins

Sample Number	Critical Flaw Type					
	Open Pore	Closed Pore	Processing Defect	Subsurface Large Grain	Machining Flaw	Undetermined
1				•		
2			•			
3						•
10						•
11						•
12			•			

TABLE 5. FLEXURE TEST RESULTS FOR MULL-ZH-HIP* (IITRI SM5)

Sample Number	4-Point Flexure Strength		Failure Strain, %	Elastic Modulus	
	psi	MPa		10 ⁶ psi	GPa

a. Strength at Various Temperatures

<u>25°C</u>					
1	39,050	269.3	0.12	32.6	224.6
2	36,550	252.0	0.11	32.8	226.3
3	42,140	290.6	0.13	32.3	223.0
Mean	39,250	270.7	0.12	32.6	224.6
<u>800°C</u>					
4	29,310	202.1	0.09	33.3	229.6
5	19,610	135.3	0.06	33.1	228.5
6	27,500	189.7	0.08	33.8	233.4
Mean	25,470	175.6	0.08	33.4	230.6

b. Fracture Origins

Sample Number	Critical Flaw Type					
	Open Pore	Closed Pore	Processing Defect	Subsurface Large Grain	Machining Flaw	Undetermined
1		•				
2		•				
3						•
4				•		
5						•
6				•		

*Billet No. T041285-2.

TABLE 6. FLEXURE TEST RESULTS FOR MULL 1:1 ZH (IITRI SM6)

Sample Number	4-Point Flexure Strength		Failure Strain, %	Elastic Modulus		
	psi	MPa		10 ⁶ psi	GPa	
a. <u>Strength at Various Temperatures</u>						
<u>25°C</u>						
1	43,990	303.3	0.14	31.8	219.3	
2	47,690	328.8	0.15	31.9	219.9	
3	52,540	362.3	0.17	32.3	222.7	
Mean	48,070	331.5	0.15	32.0	220.6	
<u>800°C</u>						
4	32,320	222.9	0.09	36.6	252.3	
5	36,950	254.8	0.10	35.9	247.8	
6	32,100	221.4	0.10	32.0	220.5	
Mean	33,790	223.0	0.10	34.8	240.2	
<u>25°C After 1000°C/140 hr Exposure</u>						
X1	33,630	231.9	0.12	29.0	199.8	
X2	32,360	223.2	0.11	29.5	203.6	
X3	41,900	288.9	0.15	28.7	197.9	
Mean	35,960	248.0	0.13	29.1	200.4	
b. <u>Fracture Origins</u>						
Sample Number	Critical Flaw Type					
	Open Pore	Closed Pore	Processing Defect	Subsurface Large Grain	Machining Flaw	Undetermined
1				•		
2						•
3				•		
4				•		
5				•		
6						•
X1	•					
X2		•				
X3						•

TABLE 7. FLEXURE TEST RESULTS FOR MULL 1:1 ZH (IITRI SM7)

Sample Number	4-Point Flexure Strength		Failure Strain, %	Elastic Modulus	
	psi	MPa		10 ⁶ psi	GPa

a. Strength at Various Temperatures25°C

1	45,510	313.8	0.14	32.7	225.5
2	38,000	262.0	0.12	32.7	225.5
3	42,120	290.4	0.13	32.7	225.5
Mean	41,880	288.7	0.13	32.7	225.5

800°C

4	21,580	148.8	0.07	31.3	214.4
5	23,560	162.5	0.07	32.8	226.0
6	22,710	156.6	0.07	32.4	223.3
Mean	22,620	156.0	0.07	32.1	221.2

b. Fracture Origins

Sample Number	Critical Flaw Type					
	Open Pore	Closed Pore	Processing Defect	Subsurface Large Grain	Machining Flaw	Undetermined
1		•				
2				•		
3		•				
4				•		
5		•				
6		•				

TABLE 8. FLEXURE TEST RESULTS FOR MULL 2A ZH (IITRI SM8)

Sample Number	4-Point Flexure Strength		Failure Strain, %	Elastic Modulus		
	psi	MPa		10 ⁶ psi	GPa	
a. <u>Strength at Various Temperatures</u>						
<u>25°C</u>						
1	38,700	266.8	0.12	32.8	226.1	
2	47,410	326.9	0.15	32.0	220.6	
3	37,360	257.6	0.12	31.6	217.9	
Mean	41,160	283.8	0.13	32.1	221.5	
<u>800°C</u>						
4	24,490	168.9	0.09	27.5	189.7	
5	30,440	209.9	0.09	31.7	218.5	
6	24,550	169.3	0.07	33.8	233.2	
Mean	26,490	182.7	0.08	31.0	213.8	
<u>25°C After 1000°C/140 hr Exposure</u>						
X1	29,880	206.1	0.10	29.8	205.8	
X2	38,000	262.1	0.13	29.6	203.8	
X3	27,860	192.2	0.09	31.0	213.5	
Mean	31,910	220.1	0.11	30.1	207.7	
b. <u>Fracture Origins</u>						
Sample Number	Critical Flaw Type					
	Open Pore	Closed Pore	Processing Defect	Subsurface Large Grain	Machining Flaw	Undetermined
1			•			
2						•
3				•		
4				•		
5						•
6				•		
X1			•			
X2				•		
X3						•

TABLE 9. FLEXURE TEST RESULTS FOR MULL 2A ZH (IITRI SM9)

Sample Number	4-Point Flexure Strength		Failure Strain, %	Elastic Modulus	
	psi	MPa		10 ⁶ psi	GPa

a. Strength at Various Temperatures25°C

1	29,960	206.6	0.09	33.9	233.7
2	27,190	187.5	0.08	33.7	232.4
3	36,720	253.2	0.11	34.0	234.4
Mean	31,290	215.7	0.09	33.9	233.5

800°C

4	15,040	103.7	0.05	31.2	214.9
5	18,740	129.2	0.06	32.4	223.5
6	14,380	99.2	0.05	29.8	205.8
Mean	16,050	110.7	0.05	31.1	214.7

25°C After 1000°C/140 hr Exposure

X1	36,960	254.9	0.12	31.2	215.5
X2	40,780	281.2	0.13	31.8	219.0
X3	39,140	269.9	0.13	30.5	211.7
Mean	38,960	268.7	0.13	31.2	215.4

b. Fracture Origins

Sample Number	Critical Flaw Type					Undetermined
	Open Pore	Closed Pore	Processing Defect	Subsurface Large Grain	Machining Flaw	
1			•			
2		•				
3			•			
4				•		
5				•		
6				•		
1X		•				
X2						•
X3				•		

TABLE 10. FLEXURE TEST RESULTS FOR MULL 2A ZH (IITRI SM10)

Sample Number	4-Point Flexure Strength		Failure Strain, %	Elastic Modulus	
	psi	MPa		10 ⁶ psi	GPa

a. Strength at Various Temperatures

25°C

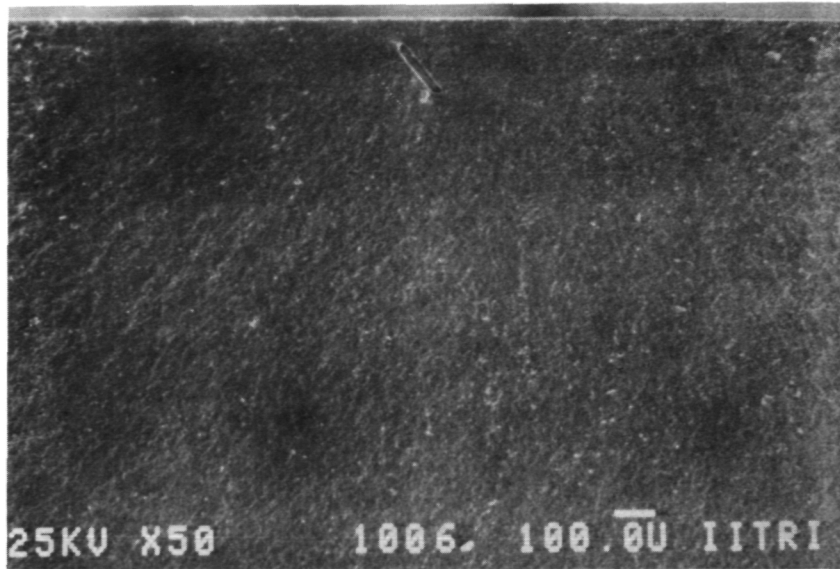
1	43,720	301.4	0.14	31.8	219.3
2	32,750	225.8	0.10	32.0	220.6
3	40,020	277.5	0.13	31.0	213.7
Mean	38,830	268.2	0.12	31.6	217.9

800°C

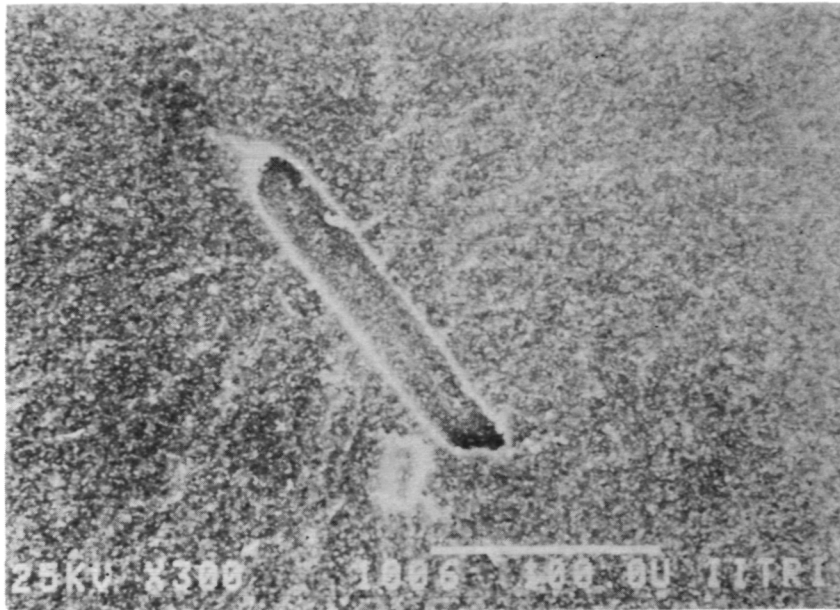
4	28,650	197.6	0.09	32.3	223.0
5	41,700	287.5	0.14	30.5	210.4
6	32,320	222.9	0.10	31.4	216.7
Mean	34,220	236.0	0.11	31.4	216.7

b. Fracture Origins

Sample Number	Critical Flaw Type					
	Open Pore	Closed Pore	Processing Defect	Subsurface Large Grain	Machining Flaw	Undetermined
1						•
2				•		
3		•				
4		•				
5						•
6		•				



- (a) Subsurface elongated pore was the fracture origin for this MULL 2A ZH, 10 v/o, (b) sample tested at 800°C (sample number SM10F6).



- (b) Higher magnification view of (a) above.

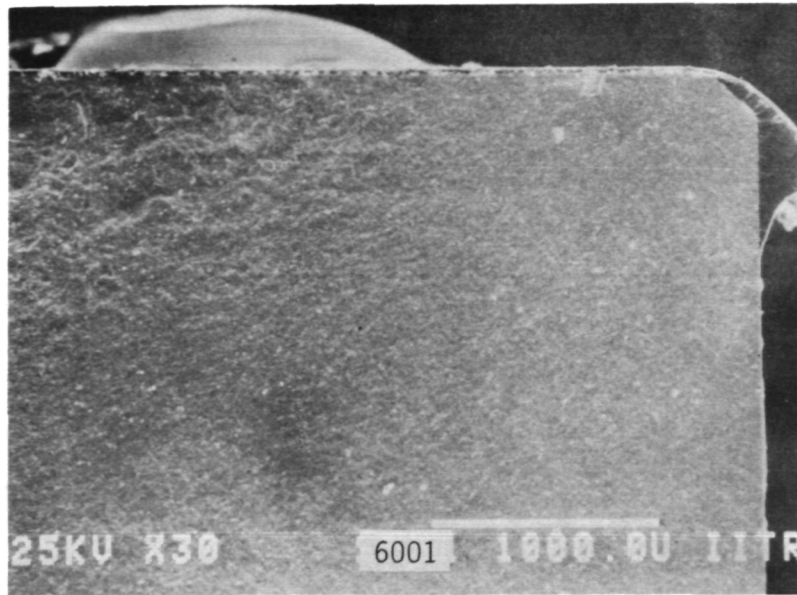
Figure 2. SEM micrographs of representative types of fracture origins (tensile surface is uppermost in each photograph) of samples tested in 4-point flexure at various temperatures.

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OF POOR QUALITY

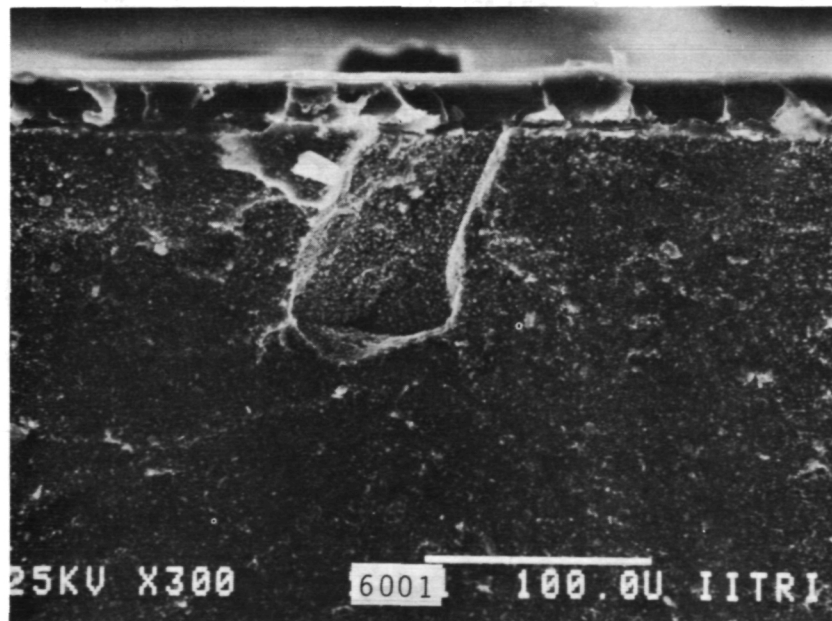


- (c) This MULL 1:1 ZH sample failed at a subsurface pore cluster in flexure at room temperature (sample number SM3F2).

Figure 2 (cont.)

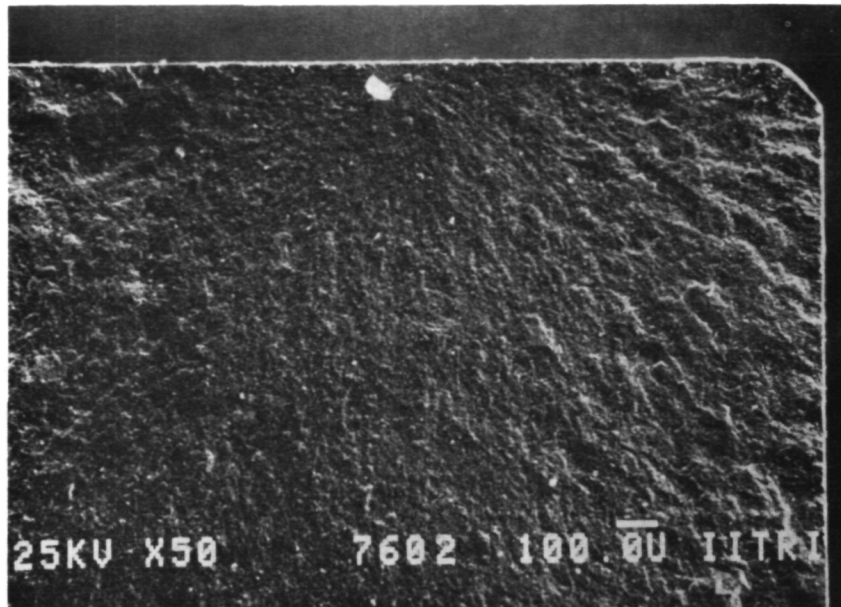


(d) Fracture surface of MULL 1:1 ZH, 15 v/o ZH tested at room temperature after 1000°C/140 hr static air exposure. An open pore was the critical flaw (sample number SM6X1).



(e) Detail of (d) above.

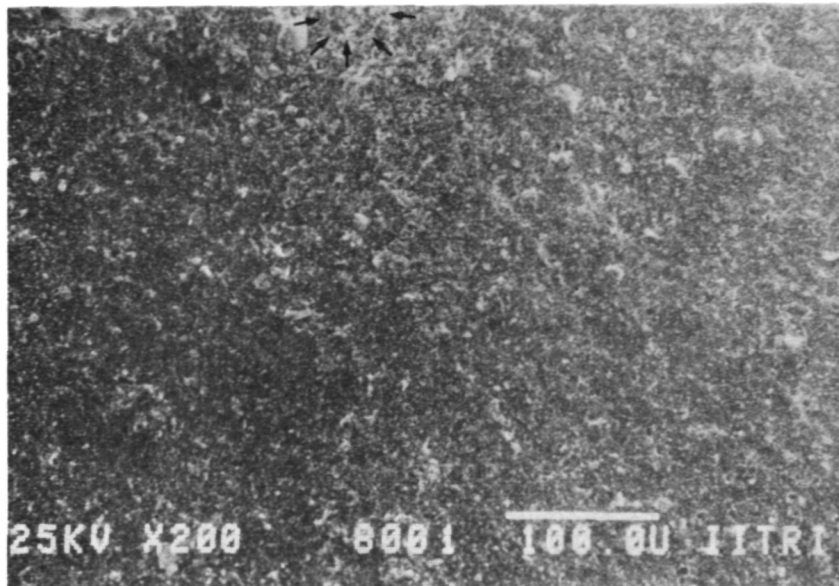
Figure 2 (cont.)



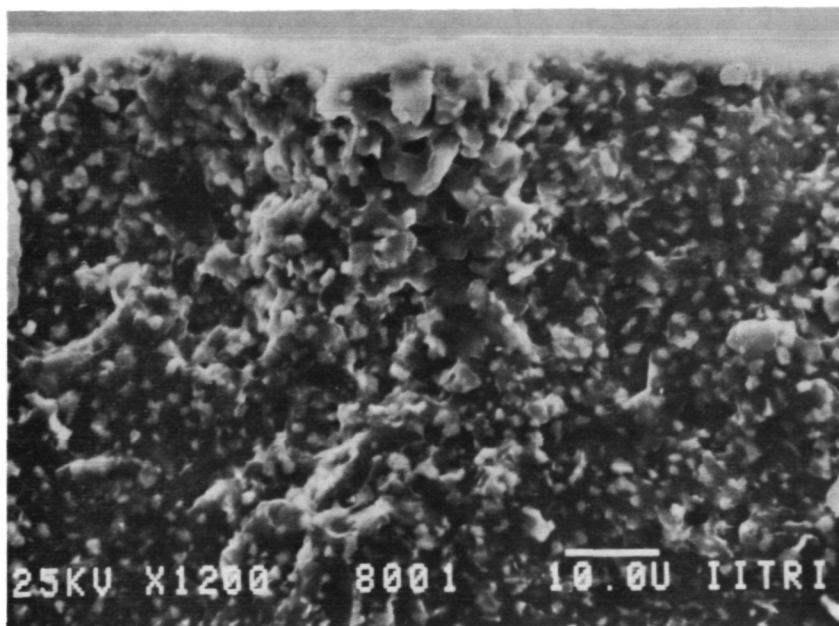
(f) A large subsurface inclusion was the fracture origin of this MULL 1:1 ZH, 10 v/o sample tested at room temperature (sample number SM7F2).



(g) A higher magnification view of (f) above. In an optical microscope such inclusions appeared glassy.



(h) This exposed (1000°C/140 hr) MULL 2A ZH, 15 v/o sample tested at room temperature had a processing defect fracture origin in the form of an incompletely sintered region at the tensile surface (sample number SM 8X1).



(i) Detail of (h) above showing the lower density region which is $\sim 20 \mu\text{m}$ diameter.

Figure 2 (concluded)

2. COMPRESSIVE STRENGTH

Compression testing was performed on one batch of material at room and elevated temperature, and at ambient temperature after static air exposure at 1000°C/100 hr. Elevated temperature testing was performed in a Kanthal wire wound furnace placed in an Instron testing machine. The load platens used for all tests were made of Udimet 700.* The upper platen fitted into a hemispherical seat in the upper load rod to give some self-alignment to the load train. At elevated temperatures, flat and parallel plates of Norton NC-132 HP-Si₃N₄ were placed between the sample and platens to lessen the chance that the small diameter sample would cause an indentation on the loading platens.

Samples were 6.35 mm diameter by 12.7 mm long. The crosshead speed was 8.5×10^{-3} mm/sec. Elastic modulus and Poisson's ratio were determined at room temperature using 2-element, 90°, "Tee" rosette resistance strain gages. Modulus was not measured at elevated temperature. The results are presented in Table 11. Compressive strength varied from 250 to 2587 MPa (36 to 375 ksi). Whether this is due to material variation or nonuniform loading during testing is not known. Samples were completely destroyed during testing (explosive brittle fracture), so fracture analysis was not possible. In the case of sample 11, the large pore (which presumably contributed to the sample's low strength) was discovered prior to testing. The low strength of sample 8 may also be the result of a similar subsurface processing defect.

*Special Metals Corp., New Hartford, NY.

TABLE 11. COMPRESSION TEST RESULTS FOR MULL 1:1 ZH* (IITRI SM11)
AT VARIOUS TEMPERATURES

Sample Number	Compressive Strength		Elastic Modulus		Poisson's Ratio
	psi	MPa	10 ⁶ psi	GPa	
<u>25°C</u>					
1	375,250	2587.3	32.6	224.7	0.29
2	144,600	997.0	--	--	--
3	122,200	842.5	26.8	184.6	--
Mean	214,120	1475.6	29.7	204.7	--
<u>800°C</u>					
4	260,710	1797.5	--	--	--
5	266,870	1840.0	--	--	--
6	132,480	913.4	--	--	--
Mean	220,020	1517.0	--	--	--
<u>1000°C</u>					
7	--	--	--	--	--
8	173,980	1199.5	--	--	--
9	52,150	359.6	--	--	--
Mean	113,065	779.6	--	--	--
<u>25°C After 1000°C/100 hr Exposure</u>					
10	177,780	1225.7	26.7	184.1	0.26
11	36,360**	250.7	--	--	--
12	137,370	947.1	13.9	95.7	0.28
Mean	117,170	807.8	20.3	139.9	0.27

*Notes on mailing package for this material were: #1 AM-5, sinter 1650/1 hr, same composition as TT052185-2, except attrition mill batch 9 hr.

**Sample contained large open pore at surface.

3. FRACTURE TOUGHNESS

Fracture toughness values, K_{IC} , were determined using a modified indentation-strength method. The objective was to observe the relative toughness of each material as a function of temperature.

The indentation-strength method of Chantikul et al.,¹ was used for this work, where strength is related to material toughness by the equation:

$$K_{IC} = \eta_V^R (E/H)^{1/8} (\sigma P^{1/3})^{3/4}$$

where: η_V^R is a dimensionless constant

E/H is the ratio of elastic modulus to hardness, GPa/GPa

σ is the indentation flexure strength, MPa

P is the indentation contact load, MN

Initial measurements were necessary to determine the proper indentation load, P . To determine the proper indentation load, samples having indentation loads of 5 to 10 kgf (4.9×10^{-5} to 9.8×10^{-5} MN) were tested in 4-point flexure at ambient temperature. An indentation load of 10 kgf (9.8×10^{-5} MN) was chosen as the one which would assure a controlled flaw large enough (relative to grain size and natural flaws) to be the fracture origin.

Indentations were made using a Vicker's Hardness test machine. They were made at room temperature, in ~40% relative humidity, just prior to flexure testing. The indentation load duration was 15 sec. The indentation axes were oriented parallel to the sample length and width. The samples were not post-indentation annealed, nor was any oil placed on the indentations, since it was felt that at elevated temperature those treatments would be ineffectual.

Table 12 summarizes the test and calculation parameters. The material toughness was calculated according to the equation above. Two assumptions were made in order to perform the calculations. First, the constant η_V^R was assumed to be 0.59, based upon the reference work^{1,2} and work done by Schioler at AMMRC on transformation-toughened zirconias.^{3,4} Second, the ratio of

TABLE 12. PARAMETERS FOR K_C CALCULATION

Samples

- 3.00 x 4.00 x 45 mm flexure bars
- As-received, as-machined surfaces

Controlled Flaw

- One Vicker's indentation at center of tensile surface
- Indentation load = 10 kg = 98N
- No post-indentation anneal
- Indentations not covered with immersion oil

Flexure Testing

- 4-point configuration
- Lower span = 40 mm, upper span = 20 mm
- All testing in air
- Relative humidity = 41%
- One break per sample

K_C Calculation

- $K_C = \eta_V^R (E/H)^{1/8} (\sigma p^{1/3})^{3/4}^*$
- $\eta_V^R = 0.59$ assumed
- E/H considered equal to 17 for all test conditions
- Fracture surfaces of all samples examined for valid failure

*Reference 1.

elastic modulus to hardness was calculated from the average modulus and hardness values and was assumed constant over the range of temperature. Lawn⁵ notes that variations of $10 < E/H < 50$ adds no more than $\pm 10\%$ error in K_C measurement. This is true primarily because E/H is raised to a small power ($1/8$) in the equation to determine K_C .

Tabular results of fracture toughness as a function of temperature are presented in Tables 13 and 14, and is plotted in Figure 3. The highest toughness, $3.8 \text{ MPa}\cdot\text{m}^{1/2}$, was exhibited by the hiped material at room temperature. At elevated temperature the MULL 2A ZH (15 v/o, SM8) material had a toughness twice that of mullite alone (i.e., 3.0 vs. $1.5 \text{ MPa}\cdot\text{m}^{1/2}$). Non-toughened mullite experienced a 35% decrease in toughness at 800°C , while the toughened materials maintained about 90% of their room temperature values. For comparison, commercially available transformation-toughened zirconias evaluated by the same method showed loss of toughness at 750°C (as compared to room temperature values) of 60% for Mg-PSZ materials and $\sim 70\%$ for Y-PSZ.⁶

TABLE 13. FRACTURE TOUGHNESS OF UNEXPOSED TOUGHENED
MULLITES DETERMINED BY THE INDENTATION-STRENGTH
METHOD AT ROOM TEMPERATURE (P = 98 N)

Sample No.	Indented 4-Point Flexure Strength		K_{IC} , MPa $\sqrt{m}^{1/2}$
	psi	MPa	
<u>MULL (IITRI SM1)</u>			
1	11,460	79.0	2.2
2	12,200	84.2	2.3
3	12,830	88.5	2.5
Mean	12,160	83.9	2.3
<u>MULL-Z (IITRI SM2)</u>			
1	16,930	116.8	3.0
2	18,200	125.5	3.1
3	17,730	122.3	3.1
Mean	17,620	121.5	3.1
<u>MULL 1:1 ZH (IITRI SM3)</u>			
1	14,570	100.5	2.7
2	16,360	112.8	2.9
3	14,290	98.6	2.6
Mean	15,070	104.0	2.7
<u>MULL 2:1 ZH (IITRI SM4)</u>			
1*	19,740	136.2	2.8
2*	20,450	141.0	2.9
3	16,030	110.6	2.9
4	17,260	119.0	3.0
Mean	18,370	126.7	2.9
<u>MULL-ZH-HIP (IITRI SM5)</u>			
1	23,940	165.1	3.9
2	23,510	162.3	3.8
Mean	23,730	163.7	3.8

*These samples were indented at P = 49N.

TABLE 14. FRACTURE TOUGHNESS OF UNEXPOSED TOUGHENED MULLITES DETERMINED BY THE INDENTATION-STRENGTH METHOD AT 800°C (P = 98 N)

Sample No.	Indented 4-Point Flexure Strength		K_{IC} , MPa \sqrt{m} / 2
	psi	MPa	
<u>MULL (IITRI SM1)</u>			
4	7,110	49.0	1.6
5	21,690	149.6	Fracture not at indentation
6	6,460	44.5	
Mean	6,790	46.8	1.5
<u>MULL-Z (IITRI SM2)</u>			
4	32,910	227.0	Fracture not at indentation
5	13,420	92.5	
6	18,210	125.6	3.2
Mean	15,815	109.1	2.8
<u>MULL 1:1 ZH (IITRI SM3)</u>			
4	13,020	89.8	2.5
5	12,150	83.8	2.3
6	13,860	95.6	2.6
-Mean	13,010	89.7	2.5
<u>MULL 1:1 ZH (IITRI SM6)</u>			
1	13,810	95.2	2.6
2	13,520	93.3	2.5
3	14,310	98.7	2.6
Mean	13,880	95.7	2.6
<u>MULL 2A ZH (IITRI SM8)</u>			
1	16,580	114.3	2.9
2	17,610	121.5	3.1
3	17,570	121.1	3.1
Mean	17,250	119.0	3.0
<u>MULL 2A ZH (IITRI SM9)</u>			
1	11,970	82.6	2.3
2	10,420	71.9	2.1
3	12,770	88.1	2.4
Mean	11,720	80.9	2.3
<u>MULL 2A ZH (IITRI SM10)</u>			
1	9,870	68.1	2.0
2	10,330	71.2	2.1
3	11,340	78.2	2.2
Mean	10,510	72.5	2.1

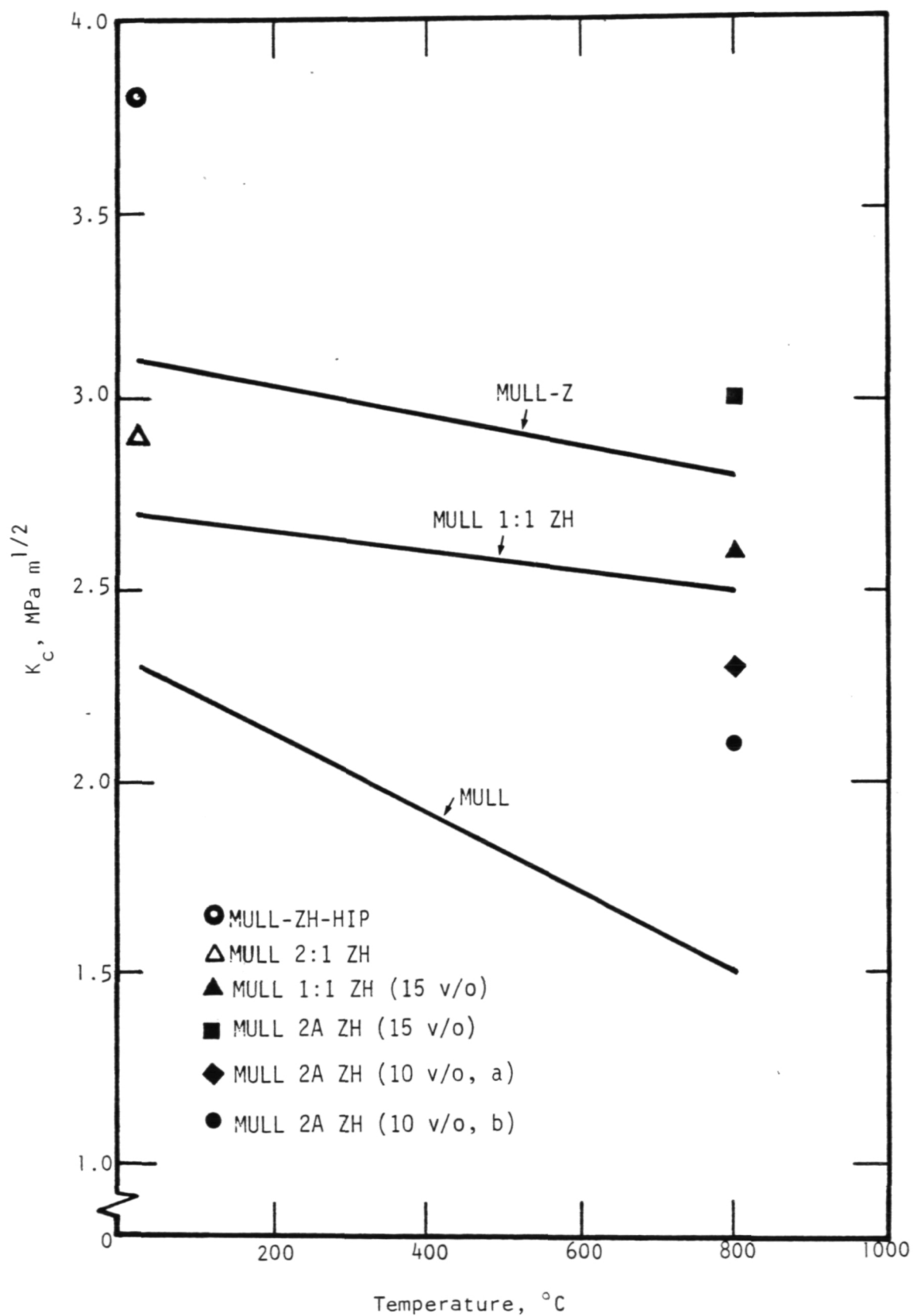


Figure 3. Fracture toughness determined by the indentation-strength method at ambient temperature and 800°C (Vickers Indentation, $P = 98 \text{ N}$).

4. SUMMARY

The toughened mullites of this study had higher strengths and K_{IC} values than non-toughened mullite. There were trends toward higher room temperature and elevated temperature strengths. Retained room-temperature strength after static soaks in laboratory air at 1000°C seemed to indicate that overaging is not a problem for this material, as with some transformation-toughened zirconias (TTZ). The elastic moduli decreased slightly as a function of temperature and exposure. Processing defects such as pores, large grains, and poorly bonded regions were the primary fracture origins. These materials are less tolerant of defects than are TTZ's; it might be expected that strengths would increase as they are removed. Compression strength was evaluated for one material, giving strengths of ~1500 MPa (220 ksi) at 25° and 800°C.

Fracture toughness was evaluated by the indentation-strength method using the same sample and fixture size as used for flexural strength evaluation. Although these toughened mullites are not as tough as transformation-toughened zirconias, they retain toughness better at elevated temperature than do TTZ materials. Strength and toughness did not always correlate well for these materials: MULL 2A ZH, 15 v/o, had the highest toughness at 800°C, but only nominal strength at that temperature. MULL 2A ZH, 10 v/o (b) had one of the highest strengths overall and retained it well at 800°C, yet had low toughness at 800°C.

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16. Abstract <p>The objective of this program is to develop an insulating structural ceramic for application in a heavy duty "adiabatic" diesel engine. The approach is to employ transformation toughening (TT) by additions of zirconia-hafnia solid solution (ZHSS). The feasibility of using ZHSS as a toughening agent in mullite and alumina has been demonstrated in the first year (Phase I) of this work. The results of the Phase I effort are documented in NASA CR-174689.</p> <p>This report covers the second year (Phase II) effort. Based on Phase I results, a decision was made to concentrate the Phase II effort on process optimization of the TT mullite. A strong factor in that decision was the low thermal conductivity and high thermal shock resistance of the mullite.</p> <p>Results of the Phase II effort indicate that optimum toughening of mullite by additions of ZHSS is difficult to achieve due to apparent sensitivity to morphology. The 48 ksi room temperature modulus-of-rupture (MOR) achieved in selected specimens is approximately 50% of the original strength target. The MOR deteriorated to 34 ksi at 800°C. The K_{IC} was measured at $3.8 \text{ MPa}\sqrt{\text{m}}$ at room temperature.</p>					
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